ΠΑΝΕΠΙΣΤΗΜΙΟ ΙΩΑΝΝΙΝΩΝ

Σχολή Θετικών Επιστημών

Τμήμα Χημείας

Μελέτη της προσρόφησης και εκρόφησης επιλεχθέντων φυτοφαρμάκων και μιας τυπικής χρωστικής σε εδαφικά συστήματα και απομάκρυνση των υπολειμμάτων τους με υψηλού κόστους (ενεργός άνθρακας) και χαμηλού κόστους υλικά, με τη χρήση στατιστικής μεθοδολογίας επιφανειών απόκρισης

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Διδακτορική Διατριβή

Ιωάννινα 2009

Adsorption-desorption study of selected pesticides and a typical dye in different soils and their removal by high cost activated carbons and low cost materials based on statistical response surface methodology

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This thesis submitted to Department of Chemistry, University of Ioannina in partial fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY (PhD)

IOANNINA, 2009

Περίληψη

Η μελέτη προσρόφησης και εκρόφησης των bromophos methyl *[O, O dimethyl - O - (2, bromophenyl 5 διχλωρο -4) phosphorothioate],* quinalphos *[O, O-diethyl O-2-quinoxalinyl phosphorothioate],* pretilachlor *[2- chloro-2’,6’-diethyl-N-(2-propoxyethyl)-acetanilide]* και μιας τυπικής χρωστικής ουσίας της congo red (CR) *[Dinatirum-3, 3΄-[[1, 1΄-biphenyl]-4, 4΄-diylbis (azo)] bis (4-aminonaphthalin-1-sulfonat)* σε πέντε εδαφικά συστήματα από διαφορετικές περιοχές της Ελλάδας και με διαφορετικές φυσικές και χημικές ιδιότητες πραγματοποιήθηκε με τη μέθοδο ισορροπίας batch. Οι ισόθερμοι προσρόφησης για όλες τις ουσίες προσαρμόστηκαν καλύτερα στην εξίσωση Freundlich από ότι στην εξίσωση Langmuir. Οι καμπύλες απόκρισης μεταξύ των διάφορων εδαφολογικών ιδιοτήτων και του συντελεστή προσρόφησης Freundlich (K_{fads}) έδειξαν ότι το περιεχόμενο οργανικό φορτίο του εδάφους παίζει καθοριστικό ρόλο στην διεργασία της προσρόφησης στα διάφορα εδαφικά συστήματα. Αντίθετα, το περιεχόμενο της αργίλου είναι αυτό που κατέχει το πιο σημαντικό ρόλο στην προσρόφηση της χρωστικής congo red. Οι ισόθερμες εκρόφησης προσαρμόστηκαν επίσης, στην εξίσωση Freundlich, ενώ το φαινόμενο υστέρησης εμφανίστηκε σε όλα τα εδαφικά συστήματα. Οι τιμές K_{fdes} αυξάνονταν με αύξηση του περιεχόμενου οργανικού φορτίου για όλα τα μελετώμενα φυτοφάρμακα ενώ για την χρωστική ουσία η μεγαλύτερη τιμή K_{fdes} παρατηρήθηκε σε εδαφικά συστήματα με το υψηλότερο ποσοστό αργίλου.

Τα φυτοφάρμακα εφαρμόζονται παγκοσμίως σε γεωργικές εκτάσεις με σκοπό την αύξηση της παραγωγής αλλά και την αύξηση της σοδιάς λόγω των μεγαλύτερων απαιτήσεων που έχει επιφέρει η αύξηση του πληθυσμού. Ωστόσο η κακή χρήση, η αποθήκευση τους ή απρόσεκτη διάθεση των άδειων περιεκτών στο περιβάλλον είναι μια από τις κύριες πηγές ρύπανσης του πόσιμου νερού παγκοσμίως. Ως επακόλουθο, η συσσώρευση των φυτοφαρμάκων στα τρόφιμα και στο πόσιμο νερό έχει γενικά αναγνωριστεί ως επικίνδυνη και η μακράς διαρκείας παραμονή τους στα υπόγεια νερά καθώς και η τοξικότητα τους είναι εν δυνάμει υπεύθυνες για διάφορες ασθένειες. Επιπρόσθετα, οι συνθετικές χρωστικές είναι απαραίτητες στις υφαντουργικές και βαφικές βιομηχανίες. Οι υφαντουργικές και οι βιομηχανίες νημάτων αποβάλλουν τα μη επεξεργασμένα απόβλητα τους στα ρέματα. Έτσι, τα επιφανειακά νερά είναι ευπρόσβλητα, η υδρόβια ζωή διακυβεύεται και οι χρήστες αντιμετωπίζουν σοβαρά προβλήματα υγείας λόγω της ρύπανσης από επικίνδυνες χημικές ουσίες που προέρχονται

από αυτές τις βιομηχανίες. Επομένως είναι επιτακτική η ανάγκη για αναζήτηση υλικών χαμηλού κόστους και ανάπτυξη μιας αποτελεσματικής μεθοδολογίας για την απομάκρυνση αυτών των οργανικών μικρο-ρυπαντών από τα απόβλητα. Η πρόσρόφηση είναι η πιο ευρέως χρησιμοποιούμενη μεθοδολογία, από τις αρχές του αιώνα, για την επεξεργασία αυτών των επικίνδυνων ουσιών από τα υδατικά συστήματα.

Στα πλαίσια της διδακτορικής διατριβής έγινε προσπάθεια απομάκρυνσης των παραπάνω επικίνδυνων ουσιών από υδατικά διαλύματα με τη βοήθεια διαφορετικών προσροφητικών υλικών που διέφεραν ως προς την προέλευση. Τα προσροφητικά υλικά που χρησιμοποιήθηκαν στην παρούσα μελέτη ήταν φύλλα τσαγιού (UTL), σκόνη φύλλων neem (NLP) και πριονίδια (SD) ως υλικά χαμηλού κόστους και ενεργός άνθρακας από κουκούτσι ελιάς (OSACs), φλοιός ρυζιού (RHACs) και υπολείμματα αποχύμωσης από ζαχαροκάλαμο (BAGACs)ως υλικά υψηλού κόστους. Αρχικά, έγινε μελέτη της κινητικής της προσρόφησης για όλα τα προσροφητικά υλικά με σκοπό να βρεθεί ο χρόνος ισορροπίας και να γίνει περιγραφή των κινητικών μοντέλων. Η στατιστική επεξεργασία των δεδομένων βασισμένη στην μεθοδολογία επιφάνειας απόκρισης (Response Surface Methodology, RSM) χρησιμοποιήθηκε για την ανάπτυξη των μοντέλων απόκρισης, ιο οποίες κατόπιν χρησιμοποιήθηκαν για την βελτιστοποίηση όλων των παραμέτρων με στόχο την επίτευξη των υψηλότερων ποσοστών απομάκρυνσης όλων των μικρο-ρυπαντών. Τέλος, προσδιορίστηκε η ικανότητα απομάκρυνσης των αναλυτών από τα προσροφητικάν υλικά μέσω των ισόθερμων προσρόφησης στις βέλτιστες συνθήκες. Τα αποτελέσματα έδειξαν ότι όλα τα προσροφητικά υλικά προσαρμόστηκαν με επιτυχία στα μοντέλα ισόθερμης τύπου Langmuir ή Freundlich, ενώ η κινητική μελέτη ακολουθεί το μοντέλο κινητικής ψευδο-δεύτερης τάξης σε όλες τις περιπτώσεις. Όλα τα προσροφητικά υλικά χαμηλού κόστους που χρησιμοποιήθηκαν στην παρούσα μελέτη είναι διαθέσιμα εύκολα αλλά και οικονομικά κατάλληλα και δεν έχουν άλλες χρήσεις. Επιπρόσθετα τα προτεινόμενα προσροφητικά υλικά δεν απαιτούν καμία προκατεργασία και έδειξαν υψηλή ικανότητα απομάκρυνσης συγκρινόμενα με τον ενεργό άνθρακα. Το μοντέλο που αναπτύχθηκε χρησιμοποιώντας την μεθοδολογία RSM μπορεί δυνητικά να χρησιμοποιηθεί και για άλλες διεργασίες, ειδικότερα σε βιομηχανικά συστήματα επεξεργασίας νερού.

Abstract

The adsorption-desorption study of bromophos methyl [*O, O- dimethyl – O - (2, 5 dichloro -4 bromophenyl) phosphorothioate*], quinalphos [*O, O-diethyl O-2-quinoxalinyl phosphorothioate*], pretilachlor [2- chloro-2’,6’-diethyl-N-(2-propoxyethyl)-acetanilide] and a typical dye congo red (CR) [Dinatirum-3, 3′-[[1, 1′-biphenyl]-4, 4′-diylbis (azo)] bis (4-aminonaphthalin-1-sulfonat) on five soils from different Greek locations with varying physical and chemical properties were studied by batch equilibration method. Adsorption isotherms fitted well to the Freundlich equation than Langmuir isotherm equation for all compounds. Regression analysis between Freundlich adsorption coefficient (K_{fads}) and various soil properties indicated that soil organic matter content plays a controlling role in the adsorption of these pesticides on the soils. But on the other hand, clay content plays an important role for congo red adsorption. Desorption isotherms also conformed well to the Freundlich equation and there was a hysteresis effect in all the soils. The Freundlich K_{fdes} values were higher for the soils with the highest organic matter percent for studied pesticides and for CR the highest Freundlich K_{fdes} was observed for the soils with the highest clay content

Pesticides are being applied to agricultural lands all over the world for increased crop production as well as for greater yield in order to meet the demand of world increasing population. However, at present, misapplication, carelessly disposal or storage of empty pesticides and containers into the environment is a major source of drinking water contamination in all over the world. As consequences, the accumulation of pesticides in food and drinking water has been generally recognized as dangerous, and the long-term persistence and toxicity of pesticides in groundwater is potentially responsible for causing various kinds of human diseases. In the same way, synthetic dyes are indispensable to the textile and dyeing industries. Textile and yarn dyeing industries are discharging their untreated waste water into the natural streams. So, the surface water body is now vulnerable, aquatic life is endangered and users are facing serious health problems due to contamination by hazardous chemicals from those industries. So it is an urgent need to search low-cost materials and efficient methodology for the removal of these pesticides and dye effluents from the waste water. Adsorption is the most widely used methodology since the beginning of this century for the treatment of these hazardous substances from aqueous matrices.

This PhD study tried to removal of above mentioned hazardous compounds from aqueous solution onto different adsorbents from diverse origin. The adsorbents used in the present study were used tea leaves (UTL), Neem leaf powder (NLP) and saw dusts (SD) as low cost materials; as well as activated carbon produced from olive seed (OSACs), rice husk (RHACs) and sugarcane bagasse (BAGACs) used as high cost materials. At first, kinetic studied were performed for all adsorbents in order find equilibrium contact time and describe the kinetic models. An approach of statistical design of experiments based on response surface methodology (RSM) was used to develop response model and desirability function was then used for simultaneous optimization of all affecting parameters in order to achieve the highest removal% of all compounds. Finally, removal capacities of all adsorbents were determined by developing isotherms, considering all optimized factors. The results indicated that all adsorbents followed either Langmuir isotherm model or Freundlich model and the kinetic study showed all data for all adsorbents fitted by pseudo-second order kinetic model. All the low cost materials used in this study are locally available as well as economically feasible and there have no alternative use, moreover, proposed adsorbents do not require any pretreatments but showed high removal capacity in compared to activated carbons. The developed model using RSM can be providing a further insight for potential use of other processes, especially industrial water treatment system.

ACKNOWLEDGEMENTS

First of all, I am very grateful to almighty Allah who has enabled me to successful completion of this work.

My especial thanks, utmost gratitude and profound appreciation to Professor Dr. Triantafillous Albanis, my honorable supervisor, for his continuous supervision, guidance, inspiration and thoughtful suggestion in completion of this work. Moreover, without his kind supervision and encouragement and logistic support I could not come up with this work. Whenever I faced any problem I ran into his office and he solved wisely. I have learnt from him how to think positively.

I would like to thank Dr. I. K. Konstantinou, Assistant professor, Department of Environmental and Natural Resources Management, University of Ioannina and Dr. A. A. Zabaniotou, Associate professor, Chemical Engineering Department, Aristotle University of Thessaloniki, for being my major advisors. Their insightful suggestions which greatly enhanced my research.

I would like to thank Dr. Vasilios A. Sakkas, Lecturer, Department of Chemistry, University of Ioannina, for his unconditional endless help and cooperation throughout my laboratory works, and his valuable time, effort and constructive comments that aided the completion of this thesis.

I also do my profound thanks to Professor P.J. Pomonis and Mr. A.P. Katsoulidis for SEM analysis and Prof. T. Vaimaikis for Zeta potential analysis. I would like to thank Mr. M. Tzoumelekas Miltos from National Agricultural Research Foundation (N.AG.REF) for soil analysis.

I would like to thank Greek State Scholarship Foundation (IKY) for providing me a full scholarship for this posts graduate study (PhD) and endless thanks to the personnel of this organization those who helped me several times in several ways.

I also want to give my profound thanks to Ms. Dimitra Lambropoulu, Lecturer, Department of Chemistry, Aristotle University of Thessaloniki, for her kind cooperation, suggestions and help during the laboratory works.

Thanks are also to all of my lab fellows Charoula Tsoutsi, Basiliki Boti, Elpiniki Amvrazi, Yiannis Zioris, Dimitris Gabriliades, Alexia Villioti, Konstantina Karametsi, Christina Kosma, Georgia Kalampoki, Nikos Petridis, Katerina Panagiotou and Nikos Spyridonakos; who taught me, helped me and support me in various ways from the very beginning to till today. For me they did the most they could. I also acknowledged them for their flexibility in working with me.

I would like to thank Mr. Apostholos Thoma and Ms. Maria Thoma for their help, encouragement and kind support during the stay in Greece.

I especially like to thank Ms. Dil-A-Raushon for sharing many of my thoughts and beliefs and encouraging me throughout the study period.

Last but not least I would like to thank all of my well wishers, friends and personnel of the Department of Chemistry, University of Ioannina, Greece, those who helped me lots in many ways.

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LIST OF SYMBOLS AND ABBREVIATIONS

^{0}C	Degree Celsius
ACs	Activated carbons
ANOVA	Analysis of variance
AOPs	Advanced oxidation processes
BAGACs	Bagasse activated carbon
BBC	British broad casting corporation
CCD	Central composite design
cm	Centimeter (100 cm=1 meter)
CR	Congo red
EC	European commission
ECD	Electron capture detector
FAO	Food and agriculture organization
FTIR	Fourier Transform Infrared Spectroscopy
g	Gram
h	Hour
HI	Hysteresis index
L	Liter
LOF	Lack of fit
mg	Milligram
min	Minute
ml	Milliliter
mm	Millimeter
NLP	Neem leaves powder
OC	Organic carbon
OM	Organic matter
OPPs	Organophosphorus pesticides
OSACs	Olive seed activated carbon
P	Statistical probability
RHACs	Rice husk activated carbon
rpm	Revolution per minute
RSM	Response surface methodology
SD	Sawdust
SEM	Scanning electron microscopy
UNEP	United Nations Environment Programme
USDA	United States Department of Agriculture
UTL	Used tea leaves
WHO	World health organization
µg	Microgram

CHAPTER I

GENERAL INTRODUCTION

1.1. Background and rationale

The use of pesticides in agriculture is worldwide the most common way of controlling pests. The world population is increasing day by day and an efficient use of pesticides is key parameters for more production of agricultural commodities as well as meeting these growing needs of huge population. For these reason, it is difficult to completely imagine the levels and security of today's yields without the use of synthetic pesticides. However, the irrational use of these products has led to serious problems in context of food, environment and human health due to the presence of pesticides in soil, ground- and surface water and air. Besides, terrestrial and aquatic ecosystems may be affected as well as altered by loss of biodiversity and destructing food chains. The fate and behavior of pesticides in the soil environment involve several different and often simultaneous phenomena including chemical, biological and photochemical degradation, transport and accumulation, volatilization and leaching, which are influenced to various extents by a number of physical, physico-chemical, biochemical, pedological and climatic factors and management practices (Konda, 2002). Like pesticides, synthetic dyes have been considered as an extremely important pollutant in environment due to their complex composition, high toxicity, poor degradability and great solubility in water. Although the role of dyes could not be ignored in aesthetic point of view. Toxic water released from several yarn dyeing and processing mills are polluting the local environment, causing myriad suffering to the adjacent people and posing serious health hazard by contaminating surface water bodies. An understanding of adsorption-desorption in the soil environment is very important for predicting the fate and behavior of organic pollutants after their application or discharge. Adsorption is a key aspect that controls the pesticides activity, mobility, persistence and environmental fate. On the other hand, desorption process determines the release rate, transformation and bioavailability of the pesticides in soil. The complexity of these phenomenons depends on the regional and temporal variation of soils and types of chemicals. The same pesticide may be behaved differently in the same organic matter content of soils outside Greece. However, this can give the approximate idea about the fate of that pesticide. Therefore, it is imperative to determine the adsorption-desorption behaviour of these organic pollutants in the soil environment in order efficient management of environment as well as crops production.

Groundwater is being depleted by the demands of megacities and agriculture, while fertilizer runoff and chemical pollution threaten water quality and public health. According to a recent report by the United Nations Environment Programme (UNEP), by 2025, two-thirds of the world's population will live in a nation that is considered water-stressed. Diseases carried in water are responsible for 80% of illnesses and deaths in developing countries, killing a child every eight seconds. Each year 2.1 million people die from diarrhoeal diseases associated with poor water (BBC, 2004). The researchers are tried to find out the way of treating this wastewater by several means. Adsorption is one of the recognized methods used in the removal of hazardous materials from polluted water among other techniques as advanced oxidation processes (AOPs), biodegradation, ozonation, coagulation etc. Therefore, it is imperative to develop feasible and cost benefit methodology and materials in order to remove these unwanted hazardous compounds from the water.

1.2. Objectives of the study

The broad objectives of this work were

- To perform an extensive literature review on adsorption-desorption of selected compounds and their removal by low cost materials and activated carbon, and adsorption principles to effectively progress the research in this area.
- To investigate the adsorption-desorption process and binding mechanisms of bromophos methyl, quinalphos, pretilachlor and congo red dye on representative five Greek soils with varying physiochemical characteristics.
- To removal of selected pesticides and dye from aqueous solution by selected activated carbon based on statistical design of experiments.
- To examine the applicability and feasibility of design of experiments for removal of some selected compounds by selected low cost materials.

CHAPTER II

LITERATURE REVIEW

2.1. Adsorption–desorption: a general overview

Adsorption is a general term that refers to the disappearance of solutes from solution with the presumption of adsorption on a solid/liquid, solid/gas and liquid/gas. According to IUPAC terminology (IUPAC, 1972), an increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase due to the operation of surface forces. Adsorption can also occur at the interface of a condensed and a gaseous phase. The converse of adsorption, i.e. the decrease in the amount of adsorbed substance is called desorption **(Figure 2.1).**

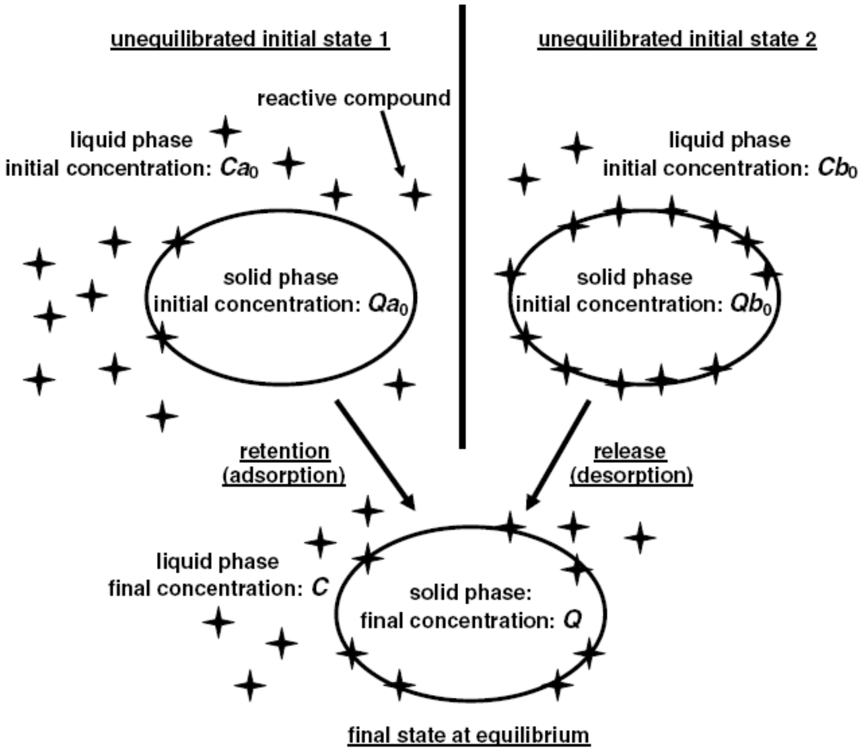


Figure 2.1. Schematic view of the adsorption and desorption phenomena (Limousin et al., 2007)

There are two general types of adsorption. One is physical adsorption and the other is chemical adsorption. Physical adsorption or van der Waals adsorption, as it is often called, is due to: orientation or dipole-dipole interactions; polarization or induced dipole interactions; dispersion interactions; ion-dipole interactions in addition to Born repulsion interactions. Chemical adsorption is due to columbic forces and results from bond formation between the adsorbent and adsorbate. A hydrogen bond may be classified under either physical or chemical adsorption, depending on whether the parameter of heat of adsorption or bond formation is taken as the major criterion for classification. Generally speaking, physical adsorption results in low heats of adsorption or low binding strength, while chemical adsorption gives high heats of adsorption or high binding strength. In physical adsorption, several monolayers may be present; while in the case of chemical adsorption. Although several monolayers may be present, only the first monolayer is chemically bonded to the surface. The other monolayers are held by dipolar attraction, and the orientation of these layers may be different from the chemically bonded first monolayer. Therefore, in summary, the innermost monolayer is chemically adsorbed whereas the other monolayers are physically adsorbed (Bailey and White, 1964).

Adsorption refers to attraction and bonding onto a surface, while absorption is a process in which the solute is taken up into a structure or across a membrane. Adsorption and absorption processes may take place simultaneously due to the heterogeneous nature of soils and sediments. The term sorption is used to describe both sorptive and adsorptive processes. The term sorbent is used to refer to the soil or sediment solids while sorbate is used to denote the chemical (contaminant) sorbed onto the solids. The solute in solution not yet sorbed is also referred to as sorptive (Grathwohl, 1997).

2.2. Adsorption Isotherms

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. A typical technique is to supply a known concentration of sorbate to a known mass of adsorbent. After the solution and solid have come to equilibrium, (at a known constant temperature and known solid to solution ratio) solution concentration is then measured and the difference between the initial concentration and final equilibrium concentration adjusted for the solution volume is assumed to be the amount of sorption per unit mass of sorbent. Mathematically

$$\text{Amount adsorbed} = \left(x/m\right)_{ads} = \left(C_0 - C_e^{ads}\right)V/W \qquad (2.1)$$

Where, *(x/m)*$_{ads}$ is the adsorbed amount (μg g $^{-1}$), C_e^{ads} and C_0 are equilibrium concentration and initial concentration (μg mL^{-1}) of the substance, V is the volume of water used (L) and W is the weight of the sample used (g).

Knowing the amount of sorbate per unit mass of sorbate *(x/m)*$_{ads}$, a plot of equilibrium concentration C_e^{ads} vs *(x/m)*$_{ads}$ is constructed. This plot is called an adsorption sorption isotherm. The name refers to the constant temperature maintained during the sorption process.

This mismatch between adsorption and desorption isotherms is called ''pseudo-hysteresis'' **(Figure 2.2)** or ''kinetic hysteresis'' (Strawn and Sparks, 1999). A more convenient term could be ''apparent irreversibility'' (Ford et al., 2002). According to IUPAC (1972), Adsorption hysteresis is said to occur when adsorption and desorption values deviate from one another. In such a case the isotherm possesses a hysteresis loop, the shape of which varies from one adsorption system to another. Hysteresis loops are mostly with mesoporous solids, where the so-called capillary condensation occurs (Dabrowski, 2001).

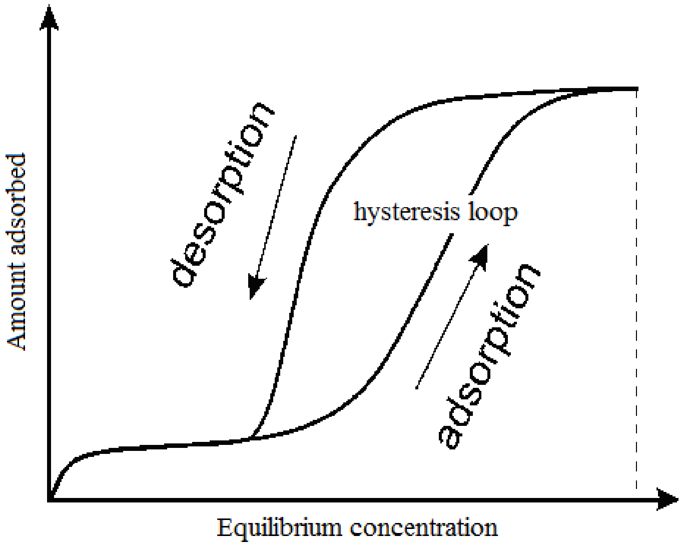


Figure 2.2. Adsorption-desorption with hysteresis

2.2.1. The four main types of isotherms

Giles et al. (1974) have proposed to classify isotherms into several categories based on initial slope which is important because it depends on the rate of change of site availability. The main four types of isotherms presented in **Figure 2.3**.

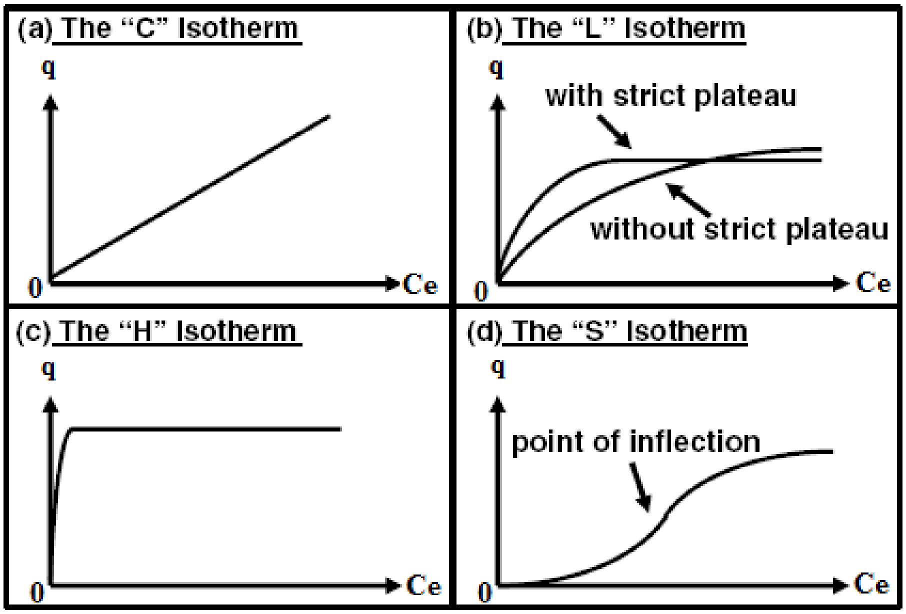


Figure 2.3. The four main types of isotherms (after Giles et al., 1974). q is the adsorbed amount and Ce the equilibrium concentration

2.2.1.1. The ''C'' isotherm

The curve is a line of zero-origin **(Figure 2.3a)**. It means that the ratio between the concentration of the compound remaining in solution and adsorbed on the solid is the same at any concentration. This ratio is usually named ''distribution coefficient'' or ''partition coefficient'' or K_d. K_d is commonly used for adsorption studies of organic compounds that can be expressed by :

K_d= concentration in the solid phase/ concentration in the solution phase

The condition of C-curves favor the porous substrate with flexible molecules and region of differing degrees of solubility for the solute and solutes with higher affinity for the substrate than for the solvent allowing easy penetration in the substrate (Calvet, 1989).

2.2.1.2. The ''L'' isotherm

The ratio between the concentration of the compound remaining in solution and adsorbed on the solid decreases when the solute concentration increases, providing a concave curve (**Figure 2.3b**). This indicates that molecules are most likely to be adsorbed in a flat position and they don't suffer a strong competition from solvent molecules (Calvet, 1989). One usually makes two sub-groups: (i) the curve reaches a strict asymptotic plateau (the solid has a limited sorption capacity), and (ii) the curve does not reach any plateau (the solid does not show clearly a limited sorption capacity). But it often appears practically difficult to know if an isotherm belongs to the first or to the second sub group (Limousin et al., 2007).

2.2.1.3. The ''H'' isotherm

This is only a particular case of the ''L'' isotherm **(Figure 2.3c)**, where the initial slope is very high. This case was observed when adsorbent surface exhibits a high affinity for the adsorbed solute (Calvet, 1989).

2.2.1.4. The ''S'' isotherm

The curve is sigmoidal and thus has got a point of inflection **(Figure 2.3d)**. This type of isotherm showed that adsorption become easier as the concentration in the liquid phase increases (Calvet, 1989). In another description by Limousin et al., (2007), this type of isotherm is always the result of at least two opposite mechanisms. Non-polar organic compounds are a typical case: they have a low affinity with clays. But as soon as a clay surface is covered by these compounds, other organic molecules are adsorbed more easily. This phenomenon is called ''cooperative adsorption'' and is also observed for surfactants.

2.2.2. Modeling of adsorption isotherms

2.2.2.1. Freundlich Isotherm

Freundlich isotherms are observed when adsorption takes place on heterogeneous surfaces. Freundlich isotherm exhibits increasing adsorption with increasing concentration, but a decreasing positive slope as equilibrium concentration increases. Many organics and inorganic follow this type of sorption behavior. This isotherm is termed the "Freundlich Isotherm". Freundlich adsorption isotherm **(Figure 2.4a)** is described by:

$$\left(x/m\right)_{ads} = K_{f_{ads}}\left(C_e^{ads}\right)^{1/n} \qquad (2.2)$$

Linearized form of Freundlich equation **(Figure 2.4b)** can be expressed by **(Equation 2.3)**

$$\ln(\mathrm{x/m})_{\mathrm{ads}} = \ln(\mathrm{K}_{\mathrm{f_{ads}}}) + \frac{1}{\mathrm{n}}\ln(\mathrm{C}_{\mathrm{e}}^{\mathrm{ads}}) \qquad (2.3)$$

where, $(x/m)_{ads}$ is the adsorbed amount (μg g $^{-1}$), K_{fads} and $1/n$ are empirical Freundlich adsorption constants. C_e^{ads} and C_0 are equilibrium concentration and initial concentration (μg mL^{-1}) of the substance.

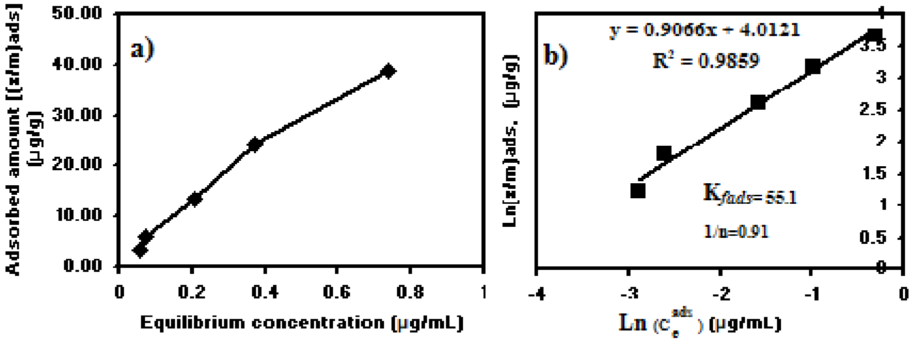


Figure 2.4. Examples of a) Freundlich isotherm and b) the linearized Freundlich isotherm.

The Freundlich desorption isotherms equation relates the content of the test substance remaining adsorbed on the soil to the concentration of the test substance in solution at desorption equilibrium **(Equation 2.4)**

$$(x/m)_{des} = K_{fdes}(C_e^{des})^{1/n} \qquad (2.4)$$

Freundlich linearized desorption isotherm also can be expressed by the **Equation 5**:

$$\ln(x/m)_{des} = \ln(K_{f_{des}}) + \frac{1}{n}\ln(C_e^{des}) \qquad (2.5)$$

$(x/m)_{des}$ is calculated as

$$(x/m)_{des} = (m_{ads} - m_e^{des})/W \qquad (2.6)$$

Where, $(x/m)_{des}$ is the substance remaining adsorbed on the soil at desorption equilibrium (μg g^{-1}), K_{fdes} is the Freundlich desorption constant. C_e^{des} is the desorption equilibrium concentration (μg mL^{-1}), m_{ads} is the amount of substance adsorbed on adsorbate at adsorption equilibrium (μg) and m_e^{des} is the amount of substance in the aqueous phase at desorption equilibrium (μg).

The value of 1/n also indicates the degree of linearity ($1/n < 1$) between solution equilibrium concentrations for adsorption and desorption.

2.2.2.2. Langmuir Isotherm

The Langmuir isotherm describes adsorption on homogeneous surface, with a maximum adsorbed amount corresponding to a monolayer and without lateral molecular attractions (Calvet, 1989). If sorption increases to a maximum value with C_e, the data will often fit an equation of the form:

$$x/m = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{2.7}$$

This formulation is called a Langmuir Equation **(Figure 2.5)**. Where, x/m is the adsorbed amount (mg g^{-1}), q_m (mg g^{-1}) is the maximum adsorption capacity of the adsorbent; C_e is equilibrium concentration (mg L^{-1}), K_a is the Langmuir's constant. If $K_a C_e << 1$, the equation is linear. As mentioned, at low concentration a Langmuir isotherm may appear to be nearly linear.

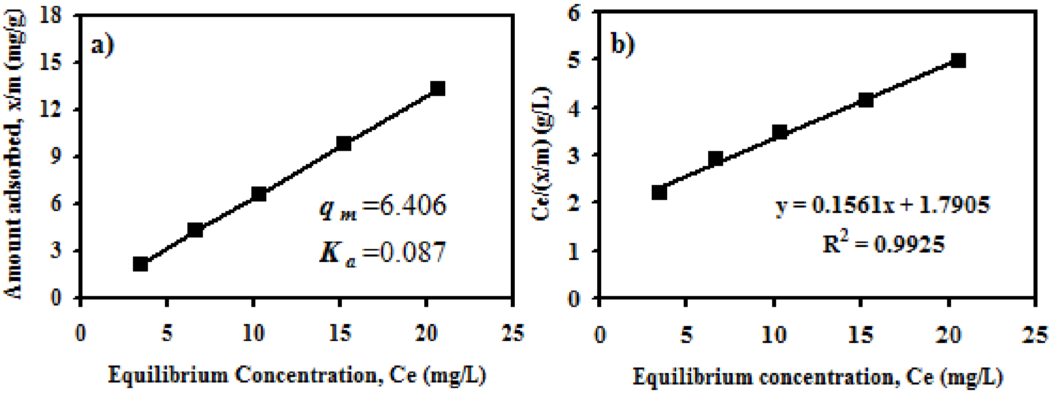


Figure 2.5. Example of a) Langmuir Isotherm and b) Langmuir linear form of the data

The non-linear form can be evaluated by transforming to the following different linear equations presented in **Table 2.1**:

Table 2.1: Langmuir isotherms and their linear forms (Kumar, 2006)

Langmuir isotherm	Different linear forms	plot
$x/m = \frac{q_m K_a C_e}{1 + K_a C_e}$	$\frac{1}{x/m} = \left(\frac{1}{K_a q_m}\right)\frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{x/m} vs \frac{1}{C_e}$
	$\frac{C_e}{x/m} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	$\frac{C_e}{x/m} vs C_e$
	$x/m = q_m - \left(\frac{1}{K_a}\right)\frac{x/m}{C_e}$	$x/m \; vs \frac{x/m}{C_e}$
	$\frac{x/m}{C_e} = K_a q_m - K_a \, x/m$	$\frac{x/m}{C_e} vs \, x/m$

2.3. Adsorption desorption process of pesticides in soils

The widespread use and the disposal of pesticides from the farmers, the institutions and the general public provide numerous sources of pesticides in the environment. After the release in the environment, the pesticides can have a lot of different fates. The pesticides that are sprayed can move itself via air and they can finally lead to other parts of environment, as to the soil or water. Pesticides which are applied directly to the soil may be washed off the soil into nearby bodies of surface water or may percolate through the soil to lower soil layers and groundwater.

Once pesticides entered into the soil environment, pesticides molecules partition between the aqueous and solid phases of the soil. The degree to which a pesticides molecules prefers one phase over the other will affect every other aspects of its behavior in soils: sorption will determine whether the pesticide will persists or not, be transported and become a pollutant or not (especially to ground water) and, often whether it will be efficacious or not (Wauchope, 2002). In general, adsorption process which controls the pesticides activity, mobility, persistence and environmental fate whereas, desorption process determines the release rate, transformation and bio-availability of the pesticides in soil (Barriuso et al., 1994; Huang et al., 1998) and all these above processes affect the quality of environmental water **(Figure 2.6).**

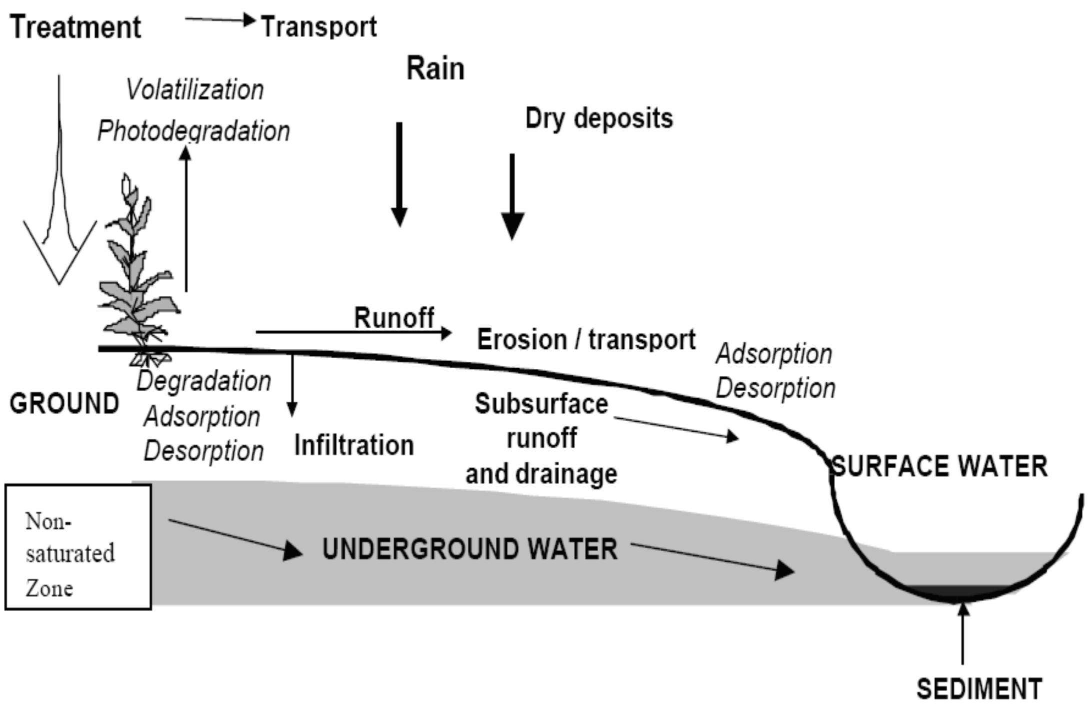


Figure 2.6. Mechanisms for transfer and transformation of pesticides in environment

2.4. Factors affecting adsorption-desorption process of pesticides by soils.

Soil is a complex mixture of various components with varying physicochemical properties. Therefore, the behavior of pesticides in soils is governed by several properties of the pesticide itself, the soil, and the soil microclimate.

2.4.1. Properties of pesticides

Soil activity and adsorption are dependent upon the chemical nature of the pesticide. The chemical nature of other materials used in formulation, such as the solvent, emulsifying agent, and surfactant, may drastically affect the interaction between the pesticide and the constituents of the soil system (Bailey and White, 1964). Basic, neutral, and acidic pesticides can all be expected to behave differently in soils. The shape and configuration of the pesticide molecule, water solubility, and charge distribution on the pesticide molecule and the adsorbent also influence a pesticide's behavior. As the solubility of a hydrophobic compound decreases, the adsorption coefficient increases, probably from entropy driven interaction with the surface. On the other hand Wang et al., (1999) found that a higher water solubility of some acetanilide herbicides corresponds to a weak tendency to adsorb on soil. Only chemicals that tend to ionize are much affected by pH, the only influence on neutral molecules would be the change in the character of the surface, For example, at low pH, humic materials are nearly neutral and more hydrophobic. Changes in pH will dramatically affect organic acids and bases by changing solubility. Cations resulting from the protonation of an organic base, for example, may more strongly sorb to soils at then the neutral species. As pH changes, surface charge also changes, and the sorption of charged species will be affected. Significant correlations have been published between the sorption coefficient (K_d) and water solubility or K_{ow} (octanol–water partition coefficient evaluating the hydrophobicity of the compound) (Karickhoff et al., 1979; Karickhoff, 1981; Gerstl, 1990; Singh et al., 1990; Barriuso et al., 1992).

2.4.2. Properties of soils

Soil properties, such as clay content and type, organic matter content, surface area, field moisture capacity, etc. play major roles in determining pesticide behavior. It has been shown that clays have a much higher sorptive capacity than do other minerals (Weber et al., 1986; Sanchez-Camazano and Sanchez-Martin, 1988; Celis et al., 1999). While organic matter content seems to exert the greatest influence (Barriuso, 1992; Morrica et al., 2000; Pusino et al., 1994) on adsorption of pesticides. In other study by Mitra et al., (2003) stated that in soils with high organic matter content, the sorption-desorption hysteresis was mainly governed by organic matter content, but in soils with low organic matter clay content played an important role. Soil structure and texture influence soil permeability (how fast the water moves through soil) as well as the amount and persistence of pesticide adsorption to soil particles. Soil pH affects both the chemical nature of the pesticide and the soil colloids and consequently pesticide behavior. Adsorbed cations in the soil influence pesticide adsorption through their ability to hydrolyze water and alter surface acidity. Many pesticide molecules cannot effectively compete with water for adsorption on soil colloids. In free solution, pesticides will be more active. Consequently, soil moisture and thus rainfall play a substantial role in pesticide behavior. Increased sorption with increased water content has been observed with atrazine (Koskinen and Rochette, 1996; Rochette and Koskinen, 1996) and metsulfuron methyl (Berglöf et al., 2003). Thus, effects of moisture content on sorption seem to be more complex when compounds are likely to be protonated in soil. Either increased water or temperature may cause some pesticides to transfer from mineral colloids to organic colloids. Since adsorption is an exothermic process, values of

Freundlich adsorption constant usually decrease with increasing temperature (Calvet, 1989). Temperature may exert an indirect influence on adsorption through its effect on solubility. In general, solubility and temperature work together to affect adsorption- that is both lead to decreased adsorption as the temperature rises (Bailey and White, 1964). Ukrainczyk and Ajwa (1996) found no significant effect of temperature, between 10° and 35°C, on primisulfuron adsorption to 23 soils. An increase in salinity can significantly lower the adsorption coefficient of cations, probably due to replacement/exchange by alkali cations. The adsorption of some acid herbicides increases with greater salinity at pH values above the pKa of the acid. Therefore pH influences the affects of salinity. Neutral molecules are generally less affected by salinity, but often show an increased adsorption with increasing salt concentration, probably due to the increase in the activity coefficient of neutral molecules and resulting decrease in aqueous solubility, i.e. salting out (Karickhoff et al., 1979). Increased salinity may also change the interlayer spacing of layer clays, as well as the morphology of soil organic matter. Chemical degradation is the breakdown of a pesticide by processes not involving a living organism. The adsorption of pesticides to the soil, soil pH levels, soil temperature and moisture all influence the rate and type of chemical reactions that occur. Many pesticides, especially the organophosphate insecticides, are susceptible to degradation by hydrolysis in high pH (alkaline) soils or spray mixes. A study by Pusino et al., (2003) observed that the highest level of Triasulfuron adsorption was measured on soils with low pH and high organic carbon content. Adsorption is probably the most important factor influencing leaching of pesticides. If a pesticide is strongly adsorbed to soil particles, it is less likely to leach. Leaching studies show that the pesticides were leached less in heavier textured soils and organic soils than in the lighter textured soils (Bailey and White, 1964).

However, reports on the adsorption behaviors of azo dyes in aqueous solution by soils are very few (Ketelsen and Meyer-Windel, 1999, Qu et al., 2008). The adsorption affinity of the dye appears to be positively correlated with the clay content of the soils and the decrease of pH or the increase of salinity can enhance the adsorption of Acid Red 14 (Qu et al., 2008).

2.4.3. Microbial Degradation

Microbial degradation occurs when microorganisms such as fungi and bacteria use pesticides as food sources. One gram of soil may contain thousands of microbes. Microbial degradation can be rapid and thorough under soil conditions favoring microbial growth. Those conditions include warm temperatures, favorable pH levels, adequate soil moisture, aeration (oxygen) and fertility. The amount of adsorption also influences microbial degradation. Adsorbed pesticides, because they are less available to some microorganisms, are more slowly degraded (Vink and van der Zee, 1995).

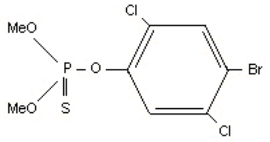
2.5. Pesticides use and their fate

The World Pesticide Sales at User Level in 1996-97 were $37,048 millions of dollars, of which herbicides accounted for the largest segment of the pesticide market (EPA, 1997). The rise in the volume of pesticides (active ingredients) in Greece was among the highest across OECD countries from 1991-93 to 2001-03 (OECD, 2008). Konstantinou et al., (2006) presented that rivers are generally found to be more polluted than lakes and Pesticides that belong to s-triazines and amide herbicides as well as organophosphorus insecticides were more frequently detected in Greek surface waters. They also found that generally, in most cases pesticides were reported in low concentrations, but in areas of high use and intensive agriculture, concentrations were more prominent. Greater pesticide use is also reported to have had an adverse impact on bird populations and damage to other biodiversity, such as wetlands, although this is poorly monitored (NCESD, 2001).

2.5.1. Bromophos methyl in the environment

Bromophos methyl [*O, O- dimethyl – O - (2, 5-dichloro -4 bromophenyl) phosphorothioate*] is a broad spectrum, non-cumulative, non-systemic halogen-containing organophosphorus insecticide **(Table 2.2)**. It is a cholinesterase inhibitor with contact and stomach action, having slight mammalian toxicity (The Agrochemicals Handbook, 1987; FOOTPRINT, 2006). Bromophos is listed in the WHO (World Health Organization) pesticides classification as an obsolete pesticide. But it is approved for use in all most all of the European countries (FOOTPRINT, 2006). Bromophos is used on various crops, mainly fruit and vegetables, for control of a large number of important sucking and chewing insect pests, such as vegetable root maggots, aphids, sawflies, fruit flies, codling moths, mangold fly and beetles. It is also used for control of stored products, as a seed protection agent for grain (The Agrochemicals Handbook, 1987).

Table 2.2. Physicochemical properties of bromophos methyl (FAO/WHO, 1994; FOOTPRINT, 2006)

Properties	Bromophos methyl
CAS registry number	2104-96-3
Chemical structure	
Chemical Formula	$C_8H_8BrCl_2O_3PS$
Molecular weight	366.1
Water solubility (mg L^{-1})	40
Vapour pressure (mPa at 20^0C)	17
Henry's constant (m^3 atm mol^{-1})	1.54×10^{-6}
Log K_{ow}	4.88
Koc - Organic-carbon sorption constant (ml g^{-1})	17

The half life of bromophos in soil has been found 88 days in laboratory conditions whereas 41 days for outdoor conditions (Bro-Rasmussen et al., 1970). Maximum Residue Limits (MRLs) of bromophos methyl for different raw agricultural Commodities have been recommended by the Joint FAO/WHO Meeting on Pesticide Residues (FAO/WHO, 1973; FAO/WHO, 1976; FAO/WHO, 1985). The Acceptable Daily Intake (ADI) for bromophos was set at 0.04 mg/kg b.w (FAO/WHO, 1978). The metabolite of bromophos most likely to be found in plants and soil is 2, 5-dichloro-4-bromophenol and small amounts of bromoxon and monodesmethyl-bromophos are also found in tomato plants (Stiasni et al., 1969). Hydrolysis and photo-degradation are the main abiotic degradation process for pesticides in aquatic and terrestrial environment. Photo-degradation of bromophos in water and soil is described by many researchers (Allmaier and Schmid, 1985; Floesser-Mueller and Schwack, 2001; Konstantinou et al., 2001; Katagi, 2004). Reports on the biodegradation and hydrolysis have also been observed (Bro-Rasmussen et al., 1970; Lartiges and Garrigues, 1995; Katagi, 2002). Different multi-residue gas chromatographic procedures were developed for determination of bromophos methyl residues from different agricultural raw commodities and water that are well documented by many researchers (Lambropoulou and Albanis, 2001; Lambropoulou et al., 2002; Lambropoulou and Albanis, 2003; Tsoutsi et al., 2006).

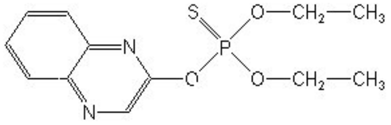
2.5.2. Quinalphos in the environment

Quinalphos (*O, O-diethyl O-2-quinoxalinyl phosphorothioate*) is an ester of phosphorothioic acid belonging to organophosphorus pesticides **(Table 2.3)**. It is moderately hazardous according to WHO (World Health Organization) hazardous classification and dangerous for the environment according to the EC (European Commission) risk classification (FOOTPRINT, 2006). It is frequently used in India, Bangladesh and all most all of the European countries for control of pests over certain crops like cotton, groundnuts, rice, tea, coffee, soybeans etc. (FOOTPRINT, 2006; Dasgupta et al., 2007; Teixeria et al., 2004; Babu et al., 1998; Agrochemicals Handbook, 1987).

Quinalphos persisted in soils with a half-life of 2 weeks and hydrolyzed to 2-hydroxyquinoxaline in soils under aerobic conditions but is further broken down to polar metabolites and carbon-di-oxides (Babu et al., 1998; Agrochemicals Handbook, 1987; Schimdt, 1972). But another study, the residues of quinalphos in soil persisted for 6–8 days depending on dose (Akter et al., 2008). Mayanglambam and Singh (2005) stated that quinalphos is moderately persistent in soil with half-life of 30 days and it is capable of leaching to subsurface soil, poses a problem of ground water contamination if present in large concentration. The increased downward mobility of quinalphos residues was detected in soil with increase in depth of soil column and persistence of organophosphate insecticides was higher as compared to carbamates in all the soil layers (Awasthi, 1984).

Photolytic degradation of quinalphos in water and soils has been depicted by many researchers (Ragnarsdottir, 2000; Goncalves et al., 2006; Dureja et al., 1988). Many studies have also been published about the toxicity of quinalphos and its metabolites on plants and soil microorganisms (Megharaj et al., 1988; Vig et al., 2006), mammals (Rupa et al., 1991; Sarkar et al., 2000; Vasilic et al., 1992) and aquatic organisms (Riediger et al., 2007; Durairaj and Selvarajan, 1992). In another study, quinalphos at levels ranging from 5 to 25 μg g^{-1} significantly increased total population of bacteria and fungi and dehydrogenase activity in soil (Gundi et al., 2005). Different multi-residue gas chromatographic procedures were developed for determination of quinalphos residues from different agricultural raw commodities and water that are well represented by many researchers (Amvrazi and Albanis, 2009; Banerjee et al., 2008).

Table 2.3. Physicochemical properties of quinalphos (FOOTPRINT, 2006)

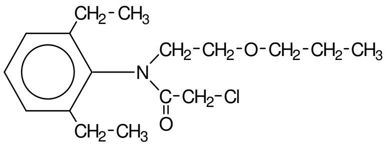
Properties	Quinalphos
CAS registry number	13593-03-8
Chemical structure	
Chemical Formula	$C_{12}H_{15}N_2O_3PS$
Molecular weight	298.3
Water solubility (mg L^{-1})	22
Vapour pressure (mPa at 20^0C)	0.346
Henry's constant (m^3 atm mol^{-1})	4.64 X 10^{-8}
Log K_{ow}	4.44
Koc - Organic-carbon sorption constant (ml g^{-1})	1465

2.5.3. Pretilachlor in the environment

Pretilachlor [2-chloro-2,6-diethyl-N-(2-propoxyethyl)acetanilide] is a chloroacetanilide herbicide **(Table 2.4)** which is widely used in transplanted and direct seeded rice (*Oryza sativa* L.) for the control of several grasses, broad-leaved weeds and sedges. The most serious weeds affecting the rice crop in Greece are barnyard grass (*Echinochloa crusgalli*) and red rice (*Oryza sativa*) and for their control, pretilachlor was introduced in 1993 (Ntanos, 2001). In Greece, The risk assessment exercise for pretilachlor use in rice also developed through different models in order to regulatory purposes (Karpouzas and Capri, 2006). Pretilachlor is used either as a pre-planting or post-emergence application. To improve its selectivity in post-emergence application, this herbicide is often mixed with the safener fenclorim.

Kawakami et al., (2007) explained that the pretilachlor adsorption on the sediment is not only influenced by the organic matter but also the mineral surface in the sediment. They also found that pretilachlor adsorption-desorption hysteresis process for the sediment was affected by the presence of organic matter in the sediment. In another study by Kibe et al., (2000) revealed that there has no correlation between the values for the Freundlich adsorption coefficient with solubilities in water, the octanol-water partition coefficients of the pretilachlor, or organic carbon contents of the studied soils.

Table 2.4. Physicochemical properties of pretilachlor (FOOTPRINT, 2006; Kanazawa, 1989)

Properties	Pretilachlor
CAS registry number	51218-49-6
Chemical structure	
Chemical Formula	$C_{17}H_{26}ClNO_2$
Molecular weight	311.85
Water solubility (mg L^{-1})	50
Vapour pressure (mPa at 20^0C)	0.133
Henry's constant (m^3 atm mol^{-1})	8.10 X 10^{-04}
Log K_{ow}	4.08
Koc - Organic-carbon sorption constant (ml g^{-1})	628

Clay contents play an important role in the adsorption of Pretilachlor (Ismail and Handah, 1999). Braschi et al., (2003) reported a strong adsorption of pretilachlor both on sediment and dissolved organic matter (DOM). They also observed that the desorption from the sediment was highly hysteretic, suggesting a strong interaction between the herbicide and the sediment organic matter. An FTIR analysis of pretilachlor-sediment complex revealed that a hydrophobic binding mechanism was involved in pretilachlor adsorption. Analysis of linear correlation regression showed that the Freundlich constant K_f (1/n) had a good correlation with soil organic matter content (OM). K_f (1/n) also correlated well with 1/Sw (solubility) and run-off would occur more easily in the soils with low OM for pretilachlor (Wang et al., 1999). According to Fajardo et al., (2000), in the 0–1 cm soil layer of the paddy field, dissipation of pretilachlor was quite rapid during the first 3 weeks but slowed down thereafter, with a DT ranging from 7 to 10 days. The herbicide was shown to leach to deeper layers (5–10 cm) within the first two weeks after the treatment and to quickly disappear afterwards. In the same study, the DT50 of pretilachlor in paddy water was about 3.5 days. In a laboratory microcosm, Flori et al., (2003) found that, 10 days after the treatment, 57.0% of the initially applied pretilachlor was still present in the surface water and 20.5% in the soil surface (0–2 cm). These amounts remained almost constant until 30 days after the treatment, showing that no degradation occurred in that time. Small amounts of pretilachlor (1.9–7.2%) were detected in deeper soil layers (2–25 cm). The degradation of pretilachlor is enhanced under conditions of increasing soil temperature and moisture levels (Ismail and Handah, 1999).

The application of pretilachlor at 1.5 kg a.i. ha^{-1} is reported to have an average efficacy of 80–90% against weedy rice (Ferrero and Vidotto, 2002). Kotula-Syka et al., (1997) demonstrated that pretilachlor degradation is promoted by micro-organism activity. Balasubramanian et al., (1999) found pretilachlor residues in rice plants when the herbicide was applied as a pre-planting treatment for two years in the same soil. Pretilachlor residues ranged between 36.2 and 29.6 $\mu g\ kg^{-1}$ in rice straw and 2.7 and 2.4 $\mu g\ kg^{-1}$ in rice grain. In soil samples, taken after harvest in the 0–15 cm deep layer, pretilachlor residues ranged between 292 and 220 $\mu g\ kg^{-1}$.

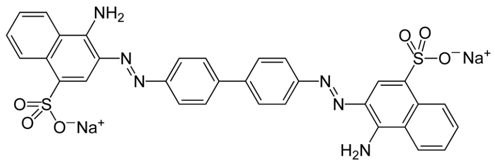
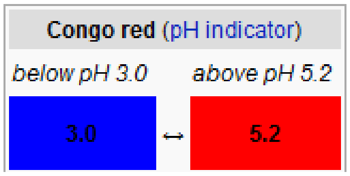
2.5.3. Congo red in the environment

Congo red (CR) [Dinatirum-3, $3^{\prime}$-[[1, $1^{\prime}$-biphenyl]-4, $4^{\prime}$-diylbis (azo)] bis (4-aminonaphthalin-1-sulfonat) is a benzidine-based anionic diazo dye and is prepared by coupling tetrazotised benzidine with two molecules of napthionic acid **(Table 2.5)**. Congo Red (CR) originated effluents produced from textiles, printing and dyeing, paper, rubber, plastics, carpet and others dye based industries (Mall et al, 2005). It is also used in medicine (as a biological stain) and as an indicator since it turns from red-brown (in basic medium) to blue in acidic one.

This congo red in the pH range of 5–10, and its sodium salt dyes cotton full red. Congo red is the first synthetic dye produced that is capable of dying cotton directly. It is very sensitive to acids and the color changes from red to blue in the presence of inorganic acids (below pH 5). This blue color may be attributed to resonance among charged canonical structures (Finar, 1986). Besides, congo red even at low concentrations is not-biodegradable and particularly toxic that affect the aquatic ecosystem as well as ground water systems and have carcinogenic and mutagenic for humans (McKay et al., 1985).

Congo red oriented waste water is a common environmental concern all over the world and researchers are tried to find out the way of treating this waste water by several means.

Table 2.5. Physicochemical properties of congo red (FOOTPRINT, 2006)

Properties	Congo red
CAS registry number	573-58-0
Color index of CR	22120
Chemical structure	
Chemical Formula	$C_{32}H_{22}N_6Na_2O_6S_2$
Molecular weight(g/Mol)	696.66
	5.5
Behavior in solution	 **Congo red** (pH indicator) below pH 3.0 above pH 5.2 3.0 ↔ 5.2
Maximum light absorption at λ_{max}(nm)	496

2.6. Removal of hazardous organic pollutants from aqueous solution onto different adsorbents: an overview

Pesticides are used to control the growth of insects, weeds, and fungi, which compete with humans in the consumption of crops. But, the ignorant or deliberate discharge of pesticides into adjacent water courses, via, for example, leaky stores, careless disposal of containers, and direct spraying, is generally causing to the surface and ground water contamination. In contrast diffuse pollution tends to arise from normal agricultural practices as pesticides make their way from their target to surface and ground waters over longer period of time. About 70,000 chemicals are on the market, with around 1,500 new ones appearing annually. At least 30,000 are thought never to have been comprehensively tested for their possible risks to people (BBC, 2004).

Ground waters tend to be at risk chiefly from the normal spraying of pesticides on land. Generally, only between 10% and 40% of pesticides applied reach their target (weeds or pests). A significant proportion remains in the soil, and this is greater for those pesticides aimed at plant roots rather than leaves. Herbicides pose the greatest risks, not only because they are applied in by far the greatest quantities, but also because they are often applied directly onto soil to kill weeds as they emerge (Foster et al., 1991), leaving them more prone to being washed away in rain.

One of the another important class of the pollutants is dyes, and once they enter the water it is no longer good and sometimes difficult to treat as the dyes have a synthetic origin and a complex molecular structure which makes them more stable and difficult to be biodegraded (Forgacs et al., 2004; Rai et al., 2005). An acute crisis of pure and clean drinking water is prevailing in the area as toxic wastes from the yarn dyeing and processing mills are mixed with the under ground water, turning water from the tube-wells yellowish. Many people are being affected with skin diseases, diarrhoea, dysentery, eye infection and nausea due to use of the water. The same picture appears everywhere in developing countries where textile effluents contaminating water bodies and posing serious threat to human health. Among the all synthetic dyes, azo dyes are mostly common used dyes for its easy synthesize. But some azo dyes possess toxic uniqueness and liable for human carcinogen and mutagen (Mall et al., 2005). Congo red (CR) [Dinatirum-3, 3′-[[1, 1′-biphenyl]-4, 4′-diylbis(azo)]bis(4-aminonaphthalin-1-sulfonat) is one of the most frequently used secondary diazo dye. Due to its benzidine based origin, it is expected to metabolize to benzidine, which is known to human carcinogen and mutagen (Mall et al., 2005). Congo red effluents are highly colored, have low biological oxygen demand (BOD) and high chemical oxygen demand (COD) while they contain high amounts of dissolved solids (Maiti et al., 2008). Moreover, due to its structural stability, this is particularly durable to biodegradation and potential threat to the environment.

Water is an essential part of any ecosystem; both in quantitative and qualitative terms, and reduced water quantity and quality both have serious negative impacts on ecosystems. Pollution of water bodies alters chemistry and ecology of rivers, lakes and wetlands. It has been estimated that about 2 million tons of waste per day are disposed of within receiving waters, including industrial wastes and chemicals, human waste and agricultural wastes (fertilizers, pesticides and pesticide residues). Although reliable data on the extent and severity of pollution is incomplete, one estimate of global wastewater production is about 1,500 km3. Assuming that 1 litre of wastewater pollutes 8 litres of freshwater; the present burden of pollution may be up to 12,000 km3 worldwide. As ever, the poor are the worst affected, with 50 percent of the population of developing countries exposed to polluted water sources (‘‘Water for People Water for Life’’ United Nations World Water Development Report, UNESCO).

From the above consequences and discussions, it is imperative to develop feasible and cost effective methodology and materials in order to remove these unwanted hazardous compounds from the waste water for better future to the humans as well as environment. For this, lots of methodologies generally adopted to treat wastewater last few decades. Among the techniques, adsorption (Lian et al., 2009; Wang and Wang, 2008; Konstantinou et al., 2000; Danis et al., 1998; Sakellarides et al., 1999), biodegradation (Binupriya et al., 2008; Hsueh and Chen, 2007; Zwiener et al., 1995) ozonation (Khadhraoui et al., 2009; Gharbani et al., 2008; Beltra’n et al., 1994), Coagulation (Dragan and Dinu, 2008; Singhal et al., 2005) and sonolysis (Sistla and Chintalapati, 2008; Song et al., 2007) and Photolytic and photocatalytic degradation (Goncalves et al., 2006; Evgenidou et al., 2006; Sakkas et al., 2005; Sakkas et al., 2004; Albanis et al., 2002) are most common and frequently used for organic pollutants removal from waste water.

Adsorption is one of the most recognized methods used in the removal of hazardous material from polluted water. The basic feature of an adsorption process is surface accumulation of material that has been described elaborately earlier. A good adsorbent (Linsen, 1970; Tien, 1994) should generally possess a porous structure (resulting in high surface area) and the time taken for adsorption equilibrium to be established should be as small as possible so that it can be used to remove dye wastes in lesser time. Some of the adsorbents are alumina, silica gel, zeolite, activated carbon, and other low cost materials.

Activated carbon is the oldest adsorbent known to effective and commercially applicable and is usually prepared from coal, coconut shells, lignite, wood etc. An extensive review by Ioannidou and Zabaniotou (2007) described the pros and cons of production methods, raw materials, process parameters, activation type and desirable use of the activated carbons. Among the two basic activation methods: physical and chemical, generally, the physical activation requires high temperature and longer activation time as compared to chemical activation, however, in chemical activation the activated carbons need a thorough washing due to the use of chemical agents. Normally it has a very porous structure with a large surface area ranging from 500 to $2000 m^2 g^{-1}$. Adsorption by the activated carbons are used as versatile adsorbents for removal of dyes (Purkait et al., 2007), metal ions (Li and Wang, 2009), phenols (Caturla et al., 1988), pesticides (Ayranci and Hoda, 2005), chlorinated hydrocarbons (Urano et al., 1991), humic substances (Lee et al., 1983), PCBs (McDonough et al., 2008), detergents (Ramírez Zamora et al., 2004) etc.

The uses of activated carbon has drawback in view of higher cost. Also, the activated carbons after their use (treatment of wastewater) become exhausted and are no longer capable of further adsorbing the dyes. Once AC has been exhausted, it has to be regenerated for further use in purifying water and a number of methods like thermal, chemical, oxidation, electrochemical are used for this purpose, the most common being thermal. It is worthwhile noting that regeneration of activated carbon adds cost, furthermore, any regeneration process results in a loss of carbon and the regenerated product may have a slightly lower adsorption capacity in comparison with the virgin activated carbon.

Therefore, it is needed to search high cost alternatives materials, which will possess some inherent characteristics of availability and sustainability. The low cost materials may be obtained from several sources and, (i) on basis of their availability, i.e., (a) Natural materials such as wood, peat, coal, lignite etc. (b) Industrial/Agricultural/Domestic wastes or by-products such as slag, sludge, fly ash, bagasse flyash, red mud etc and (c) Synthesized products; or (ii) depending on their nature, i.e., (a) Inorganic and (b) Organic.

And all these above low cost materials also used by different researcher successfully in order to removal of hazardous pollutants from waste water.

2.7. Response Surface Methodology

Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for the modeling and analysis of problems (Montgomery, 2005; Myers and Montgomery, 1995). By careful design of *experiments*, the objective is to optimize a *response* (output variable) which is influenced by several *independent variables* (input variables). An experiment is a series of tests, called *runs*, in which changes are made in the input variables in order to identify the reasons for changes in the output response. Originally, RSM was developed to model experimental responses (Box and Draper, 1987), and then migrated into the modeling of numerical experiments.

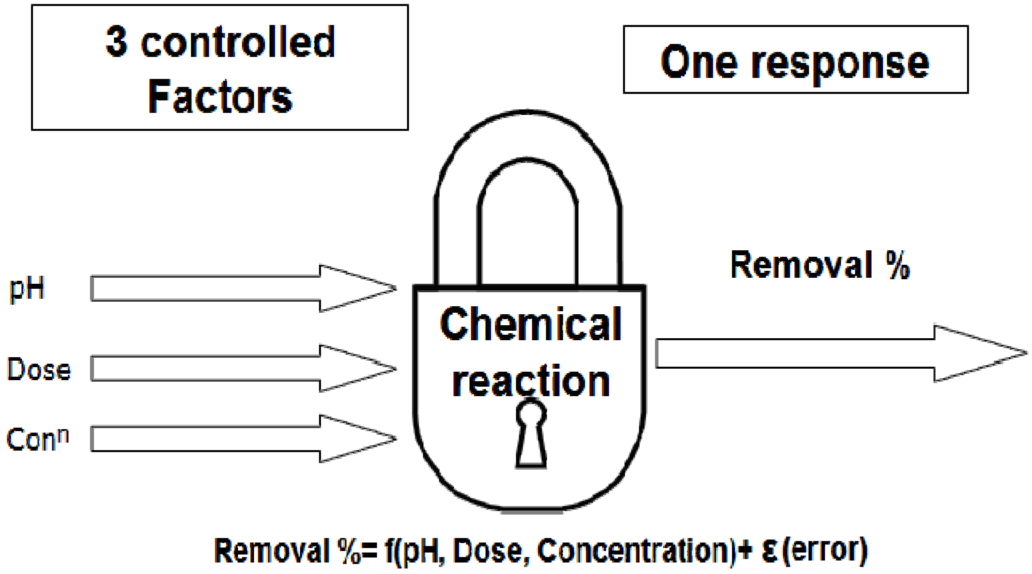


Figure 2.7. Example of 3 factors multivariate analysis for one response

For instance, suppose we wish to find the levels of three factors pH, dose and concentration that maximize the response variable removal% of a process **(Figure 2.7)**.

$$\text{Removal\%} = f\left(pH\ \ dose\ \ concentration\right) + \varepsilon\left(noise\right)$$

The surface represented by removal% = *f*(pH, dose) when other factor concentration is constant is called a *response surface*, graphically represented as a solid surface in a three-dimensional space **(Figure 2.8a).** In the *contour plot*, lines of constant response are drawn in the x_1 (pH), x_2 (dose) plane, which help visualize the shape of the response surface **(Figure 2.8b)**. Each contour corresponds to a particular height of the response surface. Such a plot is helpful in sutdying the levels of x_1 and x_2 that result in changes in the shape or height of the response surface.

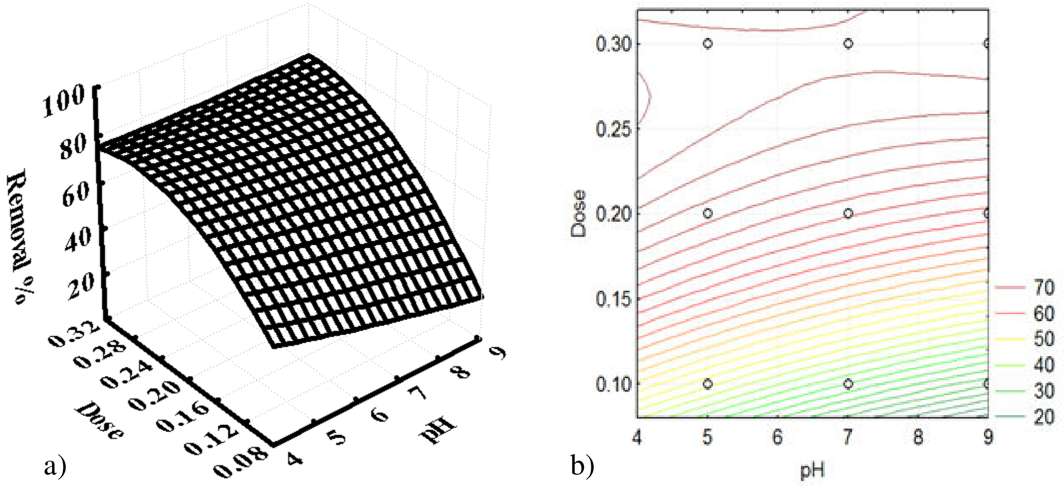


Figure 2.8. Example of (a) 3D response surface plot and (b) contour plot for the factors pH and dose when concentration is constant at his middle point

The RSM is important in designing, formulating, developing, and analyzing new scientific studying and products as well as in the improvement of existing studies and products. It is true that, the traditional one factor at a time approach to optimization is time-consuming and incompetent of achieving the true optimum condition due to lack of interactions among the factors. Besides, calculating all the effects, RSM can derive a model that represents the whole process. Therefore, now-a-days, RSM is a very popular and well established chemometric tool in almost all of the sections of chemistry (Stalikas et al., 2009; El-Masri et al., 1997; Tan et al., 2009; Li et al., 2009; Tiwari et al., 2008; Sakkas et al., 2007).

The Limitations of RSM are (a) large variations in the factors can be misleading (error, bias, no replication), (b) critical factors may not be correctly defined or specified, (c) range of levels of factors to narrow or to wide --optimum can not be defined, (d) lack of use of good statistical principles and (e) over-reliance on computer -- make sure the results make good sense.

2.7.1. Building a response surface methodology

RSM is generally conducted in three phases, as emphasized in Myers and Montgomery (2002). Phase 0 involves the screening of explanatory variables to identify those which have a significant effect on the responses, phase 1 is concerned with the location of optimum operating conditions by conducting a sequence of suitable experiments and phase 2 involves the fitting of an appropriate empirical model, usually a second-order polynomial model, in order to examine the nature of the response surface in the vicinity of the optimum. These steps are discussed elaborately below-

2.7.1.1. Factor screening experiments

The first step in developing an application or experiment as well as research is to define or specify the problem. Generally the process of determination of problem is an innately process from abstraction and approximation. Therefore it should be considered the whole procedure of designated work as well as critical steps, raw materials, equipment, costs etc. in order to obtain a holistic view of the problem.

Afterwards, selection of response(s) or output is important by considering problem analysis. For selecting response, it should be considered the sources of error and way of minimizing this error and there should also be a possible option to follow the change in response(s) in course of time.

In adsorption, our possible response(s) is to find out optimized removal% and the parameters or variables as, initial concentration of target compound, removal time, agitation speed for removal, adsorbent dose and characteristics, pH, temperature, etc. But we do not know which parameters are responsible for our expected output and these issues are difficult to resolve because the impact of the output are inter-dependent. Therefore, before selecting appropriate variables we must anticipated some valuable things. These are, possible experimental parameters to examine, reviewing and evaluating the variables on the basis of important and unimportant, Selection of experimental domain, possible interaction effects of selected parameters and not interacting parameters. Even though, it is quite difficult to carry out the experiment considering more factors due to large numbers of experiment and complex data analysis. Therefore, we have to select suitable parameters carefully for suitable output and this can be possible by vast theoretical knowledge or from review of literature or from preliminary experiments of all possible factors.

Screening is the most appropriate experimental procedure to discover suitable independed parameters or screening out invaluable parameters from many factors in order to identify those that may affect significantly on the response. The well-known Plackett-Burman (two-level fractional design) or full factorial design is usually employed for screening test (Box et al., 2005).

2.7.1.2. The path of steepest ascent/descent

The main objective of the experimenters is to estimate the current settings of factors value that are near to optimum or not. If current settiings of independent variables is not optimum then it should be aim to moving rapidly to the general vicinity of the optimum. For these, it needs some adjustment in the first order model to reach optimum setting. If first-order model shows an adequate approximation to the true surface in a small region of the interests, the method of steepest ascent procedure is followed for moving the factors levels successively along the path in the direction of true reponse as well as maximum response. The method of steepest descent is followed when minmum response is desired. The step size is determined by the prior knowledge or other practical considerations of the experimenters.

If pure curvature is detected in the first order model (significant lack of fit) then second order model should be used for solving real response suface problems.

2.6.1.3. Choice of design for RSM

The most important part of RSM is design of experiment (DOE) that have a large influence on the precision of the prediction and costs of building the response surface. Therefore, the choice of a DOE depends on the experimenter desires and willingness to expend amount of resources and the degree of control over making wrong decisions. The purpose of DOE is the selection of the points where the response should be evaluated. The common DOEs used in the RSM are full three level factorial design(3^k , where k is the number of factors), central composite design (CCD) that representing first-order (2^k) designs augmented by additional centre and axial points to allow estimation of the tuning parameters of a second-order model, Doehlert design for heterogeneous levels variables that allows a free choice of the factors to be assigned to a large or a small number of levels and Box-Behnken design for three level factor design which avoid extreme conditions of experiments.

After selection of appropriate experimental design, selection of levels of the variable should be handled carefully based on the path of steepest ascent/descent, preliminary experiments, prior knowledge of the literature review and known instrumental limitations.

2.6.1.4. Sequential mathematical model fitting

It is important to fit a mathematical model equation in order to describe the behavior of the response in the experimental domain by selected DOE. As RSM is mainly based on second order polynomial model, the experimenters should sequentially fit the first order model to second order polynomial model. The first order model will be applicable when the the approximation of true functional relationship between response and the set of independent variables has a relatively small region of interest. In other sense, first-order model uses low-order polynomial model for these reason it divulge some part of the response surface. Generally, this model is appropriate for describing a flat surface.

$$R = \beta_0 + \sum \beta_i X_i + \varepsilon \qquad (2.8)$$

In equation1, R is the reponse, β_0 is the constant term, β_i represents the coefficients of the linear parameters, X_i represents the variables and ε is the random error or noise to the response. Sometimes, it is called main effects model because it includes only the main effects of the variables.

If there has interaction terms (sometimes it is called Factor interactions or FI model, if two factors exists in the function then it can be said as 2FI model) in first order model then it can be represented as follows-

$$R = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} X_i X_j + \varepsilon \qquad (2.9)$$

where β_{ij} represents the coefficients of the interaction parameters x_i and x_j.

By adding center point in Equation 9, it can be initiates curvature into the response function but that is not sole representation of true response surface. Therefore, if first order or FI models are not adequate to the representation of true functional relationships with independent variables then a more highly structured, flexible and diversified functional forms model, such as second-order model, may be studied in order to locate the optimum point. The second order model can be expressed as follows-

$$R = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} X_i X_j + \sum \beta_{ii} X_i^2 + \varepsilon \qquad (2.10)$$

where β_{ii} represents the coefficients of the quadratic parameter.

In order to determine the adequacy of the first order and second order model, an experimenter should examine the normal plots, residual analysis, the main and interaction effects, the contour plot, and ANOVA statistics (*F*-test, *t*-test, R^2, the adjusted R^2, lack of fit).

2. 7.1.5. Optimization by desirability function

The optimization is the way of adjusting control variables in any process to find the suitable factors levels that return the best possible outcome (response).The traditional “trial-and-error" or by changing one control variable at a time while holding the rest constant, for optimization has lots of drawbacks in relating to absence of interactions effect as well as not efficient in finding the true optimum.

Generally, there have two different strategies for optimization, a) simplex optimization and b) response surface methodology. Simplex optimization is a stepwise strategy of the experiments that is performed one by one. The exception is the starting simplex in which all experiments can be run in parallel. An exact optimum can only be determined by response surface methodology, while the simplex method will encircle the optimum (Lundstedt et al., 1998). As our objective is to optimized process parameters using RSM, therefore, we will discuss optimization through RSM.

As RSM is mainly based on second-order models, so it illustrates quadratic surfaces such as minimum, maximum, ridge, and saddle. If the second-order model is found to be adequate **(Equation 2.10)**, then canonical analysis is performed to determine the location and the nature of the stationary point of the second-order model. The stationary point is the combination of design variables where the surface is at either a maximum or a minimum in all directions. If the stationary point is a maximum in some direction and minimum in another direction, then the stationary point is a *saddle point*. When the surface is curved in one direction but is fairly constant in another direction, then this type of surface is called *ridge* system (Oehlert, 2000). And all these point are calculated by a series of mathematical equations.

The visualization optimization of the predicted model equation can be obtained by the 3D surface response plot and by contour plots through determination of coordinate axes.

At present, desirability function is a popular and established technique to simultaneous determination of optimum settings of input variables that can determine optimum performance levels for one or more response. Harrington (1965) first developed the desirability function, and it was later modified by Derringer and Suich (1980) for specifying the relationship between predicted responses on a dependent variable and the desirability of the responses. The desirability procedures involve: (1) finding the levels of the independent variables that simultaneously produce the most desirable predicted responses on the dependent variables from the fitted model and (2) maximize the overall desirability with respect to the controllable factors. Therefore, the main advantages of using desirability functions are to obtain qualitative and quantitative responses by the simple and quick transformation of different responses to one measurement.

The desirability is an objective function (D) that ranges from zero (low) outside of the limits to one (maximum) at the goal. The numerical optimization finds a point that maximizes the desirability function. The characteristics of a goal may be altered by adjusting the weight or importance of the factors based on experimenter's desire. For several responses and factors, all goals transformed into one desirability function.

$$D = (d_1 \times d_2 \times d_3 ... d_n)^{1/n} = \left(\prod_{i=1}^{n} d_i \right)^{1/n} \tag{2.11}$$

where d_i indicate the desirability of the response and n is the number of responses in the measure. If any of the responses beyond the desirability, then overall function turned into zero.

It can be extended to

$$D = \left[d_1^{v1} \times d_2^{v2} \times ...... \times d_n^{vn} \right]^{1/n} \quad , 0 \le v_i \le 1 (i = 1,2.....n), \quad \sum_{i=1}^{n} v_i = 1 \tag{2.12}$$

where d_i indicate the desirability of the response y_i (i=1, 2, 3….n) and v_i represents the importance of responses. So, maximum overall desirability function D, depends on the v_i (importance) value.

2.7.1.6. Confirmation study

The confirmation study will be performed under optimized conditions and should be compare this result with the predictions. If the results (response) of confirmation experiments agree with the predictions, then we can say that developed model is robust and insensitive to external noises or tolerances by changing factors levels.

2.7.2. Box-Behnken design

The Box-Behnken design is a one type of widely used RSM approach developed by Box and Behnken (1960) for three level factors in order to fit second-order models to the response. The designs were developed by the combination of two level factorial designs with incomplete block designs **(Figure 2.9).**

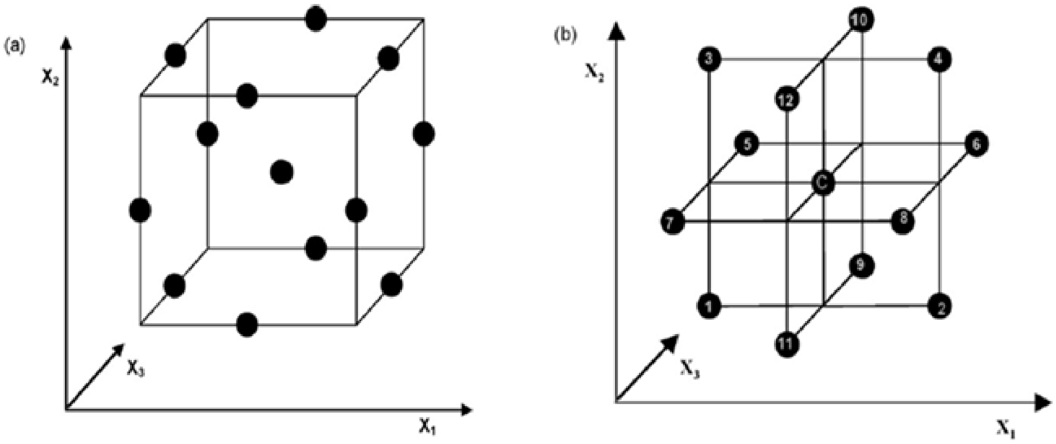


Figure 2.9. (a) the cube for BBD and (b) three interlocking 22 factorial design (Ferreira et al., 2007)

The number of experiments (N) required for the development of BBD is defined as $N=2k\ (k-1)\ +C_0$, (where k is number of factors and C_0 is the number of central points). For comparison, the number of experiments for a central composite design is $N=2k\ +2k\ +C_0$.The advantages of Box-Behnken designs include the fact that they are all spherical designs and require factors to be run at only three levels. The designs are also rotatable or nearly rotatable. Some of these designs also provide *orthogonal blocking*. Thus, if there is a need to separate runs into blocks for the Box-Behnken design, then designs are available that allow blocks to be used in such a way that the estimation of the regression parameters for the factor effects are not affected by the blocks. In other words, in these designs the block effects are orthogonal to the other factor effects. Yet another advantage of these designs is that there are no runs where all factors are at either the +1(highest) or -

1 (lowest) level. So these designs are useful in avoiding experiments performed under extreme conditions, for which unsatisfactory results might occur (Ferreira et al., 2007).

Application of Box-Behnken design in the various field of chemistry has been described intricately by Ferreira et al., (2007). Box-Behnken design has also been successfully employed in waste water treatment and removal of hazardous compounds from water by several researchers. Recently, Eker and Kargi (2008) adopted Box-Behnken design for COD, 2,4,6-trichlorophenol (TCP) and toxicity removal from synthetic wastewater in a rotating perforated-tubes biofilm reactor. A study by Tony et al. (2008) examined aluminium-based drinking water treatment sludge using Fenton reagent (Fe^{2+}/H_2O_2) by using Box-Behnken design. The adsorption of direct dye on chitosan was investigated to assess its efficiency in the treatment of waste water streams from dye works based on Box-Behnken design methods (Annadurai, 2000). Advanced oxidation of diuron in aqueous solution by photo-Fenton treatment was investigated by batch experiments with parameters considering, the concentrations of pesticide (diuron), hydrogen peroxide (H_2O_2), and ferrous ion [Fe (II)] by using Box-Behnken statistical experiment design and the response surface methodology (Catalkaya and Kargi, 2008). A Box-Behnken design was also performed to evaluate the effect of initial dye concentration, initial solution pH and temperature for the removal of Astrazon Red (Basic Red 46) and Sirius Blue (Direct Blue 85) onto aqueous solution of sepiolite (Santos and Boaventura, 2008.).

2.7.3. Central Composite Design (CCD)

The central composite design (CCD) is a design widely used for estimating second order response surfaces. It is perhaps the most popular class of second order designs. Central composite designs are two level full factorial (2^k) or fractional factorial (2^{k-f}) designs augmented by a number of center points and other chosen runs. These designs are such that they allow the estimation of all the regression parameters required to fit a second order model to a given response.

CCD consists of a $2k$ factorial runs with $2k$ axial runs and C_0 center point runs. The total number of experimental points needed (N) is determined: $N=2^k+2k+C_0$, where k is the number of variables and C_0 is the number of center points **(Figure 2.10).**

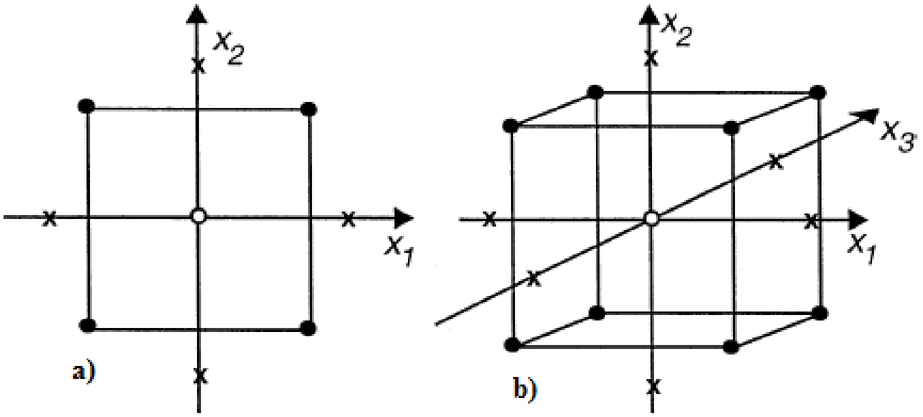


Figure 2.10. a) Central composite designs for two variables and b) Central composite designs for three variables. Markings indicating (●) factorial design,(○) centre point and (╳) axial points

The distance of the axial points from the center point is denoted by α and is always specified in terms of coded values that are stated in **Table 2.6.**

Table 2.6. Values of α with variables

Number of variables	2	3	4	5 2^{5-1}	5	6	6 2^{6-1}
Number of experiments in the factorial design	4	8	16	32	16	64	32
Number of axial points	4	6	8	10	10	12	12
Value of α	1.414	1.682	2.000	2.378	2.000	2.828	2.378

Since introduced by Box and Wilson (1951), the CCD has been studied and used by many researchers in the different arena chemistry. Delgado-Moreno et al., (2009) studied the disposal of natural, composted and vermicomposted olive cake for modifying the fate of triazine herbicides with different physicochemical properties (terbuthylazine, cyanazine, simazine and prometryn) by using CCD. Optimization of amino acid separation by reverse-phase HPLC was studied by Gheshlaghi and coauthors (2008) based on CCD. Lin et al., (2008) well used the center composite design based on response surface methodology in the optimization of methylparaben photocatalytic degradation process parameters (pH, TiO2 loading, oxygen concentration and light flux). The applied central composite design was consisted of 28 experiments divided into three blocks: (a) four variables (n = 4) at two levels: low (-1) and high (+1), full factorial design 2^4 (all possible combinations of codified values +1 and -1); (b) 8 (2n) axial points located at the center and both extreme levels; (c) 4 central replicates of the central points. In the recent study by Calza et al.(2008) followed the central composite design (CCD) to analyze the simultaneous effect of H_2O_2, Fe(II) and TiO_2 in the photocatalytic degradation of imipramine in aqueous solution. A 2^4 full factorial central composite design was successfully employed for Decolourization of Verofix Red (Reactive Red 3GL) and Lanasyam Brown Grl (Acid Brown 29) from aqueous solution by adsorption technique using a hybrid adsorbent that was prepared by pyrolysing a mixture of carbon and flyash in 1:1 ratio (Ravikumar et al., 2007).

CHAPTER III

ADSORPTION-DESORPTION STUDY OF BROMOPHOS METHYL, QUINALPHOS, PRETILACHLOR AND A TYPICAL DYE CONGO RED ON GREEK SOILS

Abstract

The adsorption and desorption of bromophos methyl, quinalphos, pretilachlor and congo red dye on five soils from different Greek locations with varying physical and chemical properties was studied by batch equilibration method. Adsorption isotherms fitted well to the Freundlich equation. The adsorption capacity of the soils for congo red was higher than other compounds studied. Freundlich adsorption coefficient (K_{fads}), showed significant correlation with soil organic matter for all pesticides, indicating that soil organic matter content was the main controlling factor for the adsorption of these pesticides on the soils. On the other hand, clay content mainly governed the adsorption of congo red in soils. Desorption isotherms also conformed well to the Freundlich equation and the highest hysteresis effect (the lowest HI) was observed in soil 1 which also had the highest organic matter content whereas the lowest hysteresis effect (the highest HI) was observed in the lowest organic matter contained soil for all pesticides. For congo red, the highest hysteresis effect (the lowest HI) was observed in soil 5 which also had the highest clay content, on the other hand, the lowest hysteresis effect (the highest HI) was observed in the lowest clay contained soil.

3.1. Introduction

The contamination of soils, groundwater and surface water by synthetic chemicals is currently a momentous concern through out the world for the reason that these compounds are detrimental to both human life and environment as well as terrestrial and aquatic ecosystems. When these organic compounds as well as pesticides are introduced into the environment through spraying on crops or discharge, the first process that occurs is adsorption, resulting the distribution of compound into soil-adsorbed and soil-solution phase. The compound that is present in soil-solution phase is bioavailable and may also be subjected to various dissipation processes such as degradation, volatilization and leaching or transported to various environmental compartments (FAO/WHO, 1996). The adsorbed pesticide is not available for theses process. But when soil-solution decreases, fraction of adsorbed pesticides may be desorbed from the soils. Sometimes due to the bioavailability, the toxicity of parent pesticides and their degradation products is making these chemical substances a potential hazard to the environment. By this way, adsorption process regulates the pesticides behaviour in soil environment. Moreover, agricultural use of such chemicals necessitates evaluation of the risks to ground water from movement of these compounds through the soil. Under field conditions, many factors may affect this process, including the applied dose, the amount and distribution of rainfall, and the soil type (structure, texture, organic carbon content), as well as xenobiotic characteristics (water solubility and volatility)(Sanchez-Martin and Sanchez-Camazano, 1991; Arienzo et al., 1994; Mandal and Adhikari, 1997). Therefore, it is imperative to study the adsorption-desorption behaviour of different organic compounds on soils.

This study carried out on two organophosphorus pesticides {bromophos methyl[O, O- dimethyl – O - (2, 5 dichloro -4 bromophenyl) phosphorothioate] and quinalphos [O, O-diethyl O-2-quinoxalinyl phosphorothioate]}, herbicides {pretilachlor [2- chloro-2’,6’-diethyl-N-(2-propoxyethyl)-acetanilide]} and a typical dye {congo red (CR) [Dinatirum-3, 3′-[[1, 1′-biphenyl]-4, 4′-diylbis (azo)] bis (4 aminonaphthalin-1-sulfonat)}. Bromophos methyl is a broad spectrum, non-cumulative, non-systemic halogen-containing organophosphorus insecticide. Bromophos methyl is used on various crops, mainly fruit and vegetables, for control of a large number of important sucking and chewing insect pests, such as vegetable root maggots, aphids, sawflies, fruit flies, codling moths, mangold flies and beetles. It is also used for stored products, as a seed protection agent for grain (The Agrochemicals Handbook, 1987). Quinalphos (O, O-diethyl O-2-

quinoxalinyl phosphorothioate) is an ester of phosphorothioic acid belonging to organophosphorus pesticides. It is frequently used for control of pests over certain crops like cotton, groundnuts, rice, tea, coffee, soybeans etc. (The Agrochemicals Handbook, 1987). Pretilachlor [2-chloro-2,6-diethyl-N-(2-propoxyethyl)acetanilide] is a chloroacetanilide herbicide which is widely used in transplanted and direct seeded rice (Oryza sativa L.) for the control of several grasses, broad-leaved weeds and sedges (The Agrochemicals Handbook, 1987). Congo red (CR) is a benzidine-based anionic diazo dye (Mall et al., 2005) and the first synthetic dye produced that is capable of dying cotton directly. It is also used in medicine as a biological stain and as a dye indicator.

Although bromophos methyl and quinalphos were with drawn from EC member-states since 2003 (Directive 2002/2076/EC) and pretilachlor since 2004 (Directive 2004/129/EC) but residues of these pesticides are still detected in food commodities and water resources (Knezevic and Serdar, 2009; Amvrazi, and Albanis, 2009; Manikandan et al., 2009; Roche et al., 2009; Villaverde et al., 2008;). This was attributed to unauthorized use of available stocks or illegal imports from non-EC member states where these compounds are available at reduced cost (Vryzas et al., 2009). The extensive literature review in previous chapter reveals that no detailed studies are available on the sorption-desorption of bromophos methyl, quinalphos, pretilachlor and congo red dye.

3.2. Objectives of the study

The aim of this work were

- to study the adsorption-desorption behavior of quinalphos and bromophos methyl in a variety of soils originated from Greece with different physical and chemical characteristics.
- to fit the adsorption-desorption data in isotherm model in order to describe the adsorption processes of the investigated compounds and to calculate physicochemical parameters of equilibrium obtained from isotherms.
- to study the mean percent balance of adsorbed and desorbed amount of compounds by soils.

3.3. Materials and methods

3.3.1 *Chemicals and Soils*

The pesticides bromophos methyl (99.1% purity), quinalphos (98.9% purity), pretilachlor (99%) were of residue analysis grade and purchased from Riedel-de Haen (Germany) and

CR dye was purchased from Riedel-de Haen (Switzerland). The physicochemical properties of the selected compounds presented in section 2.5. All other chemicals, solvents and salts were of the highest purity level supplied by Merck pro-analysis or Lab Scan, Pestiscan.

Five soil samples were collected from different agricultural areas of Greece (Tirfi Ioannina, N. Malgara, Preveza, Orestiada and Kozani) with no previous history of pesticides use. The soils were sampled from the surface layers (0 – 20 cm), then air dried and sieved to pass through a 2-mm mesh for further use. Soil pH values were measured in slurries made at a soil: water ratio of 1:1 (USDA, 1995). Organic carbon content (% OC) of the soils was determined by Walkley-Black method and the total organic mater content (% OM) was calculated by using **Equation 3.1**.

$$(\% \text{ OM}) = 1.72 \text{ X } (\% \text{ OC}) \qquad (3.1)$$

Precautions were taken to avoid contamination during sampling, drying, grinding and storage. Selected properties of the test soils are listed in **Table 3.1**.

Table 3.1. Characteristics and composition of the soil samples

Soil	Location	Soil Texture	%OM	%OC	Sand	Silt	Clay	pH
1	Tirfi Ioannina	Sandy Loam	5.49	3.19	67	29	4	6.6
2	N.Malgara	Sandy Loam	2.18	1.27	55	31	14	7.4
3	Preveza	Sandy Loam	1.98	1.15	75	11	14	5.5
4	Orestiada	loam	1.91	1.11	45	31	24	7.8
5	Kozani	Clay	0.70	0.41	24	28	48	7.7

3.3.2 *Adsorption-desorption experiment*

The batch adsorption experiments were carried out in three replicates using 15 ml polypropylene centrifuge tubes containing 1.0 g of soil and 10 ml 0.01M $CaCl_2$ solution of bromophos methyl or quinalphos or pretilachlor at different concentrations levels (0.5, 1.0, 2.5. 5.0 and 10.0 μg mL^{-1}). For congo red 50 ml polypropylene centrifuge tubes containing 5.0 g of soil and 25 ml 0.01M $CaCl_2$ solution at different concentrations levels (25, 50, 75. 100 and 125 μg mL^{-1}) were followed. CR is highly soluble in water and for better calibration, high concentration ranges were used. The $CaCl_2$ (0.01 M) was used as the background electrolyte in order to maintain the ionic strength (Yu and Zhou, 2005). To evaluate interference due to soil, an adsorption test with $CaCl_2$ (0.01M) solution but without analytes was carried out as described below. Besides, blank samples (no soil added) indicated that losses due to adsorption onto polypropylene centrifuge tubes were negligible. According to the kinetic experiments, adsorption equilibrium was reached within 24 h equilibration period (Konstantinou and Albanis, 2000). The centrifuge tubes prepared as above, were subsequently capped and shaken in a wrist action shaker for 24 h at room temperature. At the end of the apparent equilibration period the samples were centrifuged at 4500 rpm for 5 min, and the concentration of target analytes was determined in the supernatant.

Desorption in water was studied in the same soils used for adsorption. After adsorption, the supernatant was carefully decanted and was replaced with 10 ml and 25 ml of fresh 0.01M $CaCl_2$ solution for pesticides and dye respectively. The centrifuge tube was capped and shaken for a further 6 h (Konstantinou and Albanis, 2000) and centrifuged as described above, and then the supernatant was analyzed for target compounds.

A second desorption step was carried out in the same soils after desorption with water, using 10 ml of acetone and shaking for 30 min.

3.3.3. *Extraction and analysis of pesticide and dye*

For residue analysis, 5 ml of supernatant, each after adsorption and desorption, was extracted twice with 2.5 ml n-hexane using a vortex for 1 min. In the combined extracts a small amount of anhydrous Na_2SO_4 was added to remove residual water. The acetone desorption phase was filtered through glass wool fiber, containing anhydrous Na_2SO_4 as a part of clean up procedure for the samples. An aliquot of 1.0 μL of the *n*-hexane and acetone extract was injected into a Shimadzu 14B gas chromatograph equipped with ^{63}Ni electron capture detector (ECD) at 300^0 C. A DB 1 column (J & W Scientific, Folsom, CA, USA), 30 m of length, 0.32 mm i.d., coated with dimethylpolysiloxane of a film thickness of 0.25 µm was used. The temperature program was: from 80 ^{0}C (2 min) to 290^0 (10 min) at 21^0C min^{-1}. Injector temperature was set to 250 ^{0}C and the injector mode was splitless. Helium and nitrogen was used as the carrier (1.5 mL min^{-1}) and the make-up (35 mL min^{-1}) gases, respectively. Under these conditions, retention times of bromophos methyl, quinalphos and pretilachlor were 11.10, 11.48 and 13.33 minutes respectively. Ethion was used as an internal standard (IS). The recovery obtained with the extraction method used was greater than 90% for all pesticides investigated **(Table 3.2).**

Table 3.2. Retention times, detection limits and recoveries of different pesticides studied by the measurement method used in this study

Compound	**Retention time**	**Lod(mg Kg^{-1})**	**Recovery%**
Bromophos methyl	11.10	0.008	90
Quinalphos	11.48	0.008	90
Pretilachlor	13.33	0.002	93

Calibration curve of congo red was prepared by measuring absorbance of different predetermined concentrations of the samples at $\lambda_{\max}$ 496 nm using UV–vis spectrophotometer (Jasco, V-530, Japan).

3.3.4. *Data analysis*

The experimental adsorption data have been analyzed by the linearized Freundlich and Langmuir equations **(Equation 3.2 and 3.3)**

$$\ln X_{ads} = \ln(K_{f_{ads}}) + \frac{1}{n}\ln(C_e^{ads}) \tag{3.2}$$

$$\frac{1}{X_{ads}} = \frac{1}{C_e^{ads} K_a Q_{\max}} + \frac{1}{Q_{\max}} \tag{3.3}$$

X_{ads} is calculated using **Equation 3.4**

$$X_{ads} = \left(C_0 - C_e^{ads}\right) V/m \tag{3.4}$$

where, X_{ads} is the adsorbed amount (μg g $^{-1}$), K_{fads} and $1/n$ are empirical Freundlich adsorption constants. C_e^{ads} and C_0 are equilibrium concentration and initial concentration (μg mL^{-1}) of the compounds, K_a is the Langmuir constant *and* Q_{max} is the maximum adsorption capacity (μg g $^{-1}$) , V is the volume of water used (L) and m is the weight of the sample used (g).

Desorption isotherms were also fitted to the linearized Freundlich equation (**Equation 3.5**)

$$\ln X_{des} = \ln(K_{f_{des}}) + \frac{1}{n}\ln(C_e^{des}) \qquad (3.5)$$

X_{des} is calculated as

$$X_{des} = (m_{ads} - m_e^{des}) / m \qquad (3.6)$$

Where, X_{des} is the compound remaining adsorbed on the soil at desorption equilibrium (μg g^{-1}), K_{fdes} is the Freundlich desorption constant. C_e^{des} is the desorption equilibrium concentration (μg mL^{-1}), m_{ads} is the amount of compound adsorbed on soil at adsorption equilibrium (μg) and m_e^{des} is the amount of compound in the aqueous phase at desorption equilibrium (μg).

The value of 1/n also indicates the degree of linearity ($1/n < 1$) of the isotherms.

The variation of standard free energy (ΔG^0) of adsorption and desorption was calculated for each soil from the value of K_{om} using the equation

$$\Delta G^0 = -RT \ln K_{om} \qquad (3.7)$$

where, ΔG^0 is the free energy change (Kcal/mol), R is the gas constant (1.986 cal/K mol) and T is the absolute temperature ($273+25^0$C= 298 K).

The calculation of percent balances of bromophos methyl, quinalphos, pretilachlor and congo red for five different concentrations were determined according to the following calculation (Konstantinou and Albanis, 2000).

[Initial amount]= [Free amount] + [Adsorbed amount]

The adsorbed amount was determined as follows:

[Adsorbed amount]= [Desorbed amount with water] + [Desorbed amount with acetone] + [Non-desorbable amount]

The non-desorbable amount is calculated from the difference between adsorbed amount and the sum of the desorbed with water and acetone amounts. Non-desorbable amount could be also expressed as permanent adsorbed (remained) or non extractable residues.

Finally, regression analysis with analysis of variance (ANOVA) was done for every cases of K_{fads} value with different soil parameters to find the significant interactions by Minitab® 11.2, 32 bit statistical software.

3.4. Results and discussion

3.4.1. *Adsorption isotherms*

Adsorption isotherms for bromophos methyl and quinalphos in soils are presented in **Figure 1** and **Figure 2**. The adsorption data for the all compounds showed good linearity and were successfully described by the linear forms of the Freundlich and Langmuir equations. However, R^2 value by itself cannot express the good fit of the data to the above equations. Thus, the error function (Arenas et al., 2007) was calculated in order to assess which model best describes our adsorption data. Error function can be expressed as (**Equation 3.8**):

$$F_{error} = \sqrt{\frac{\sum_i^p \left(\left(q_i cal - q_i \exp\right)/ q_i \exp\right)^2}{p}} \tag{3.8}$$

where, q_i *cal* is each value of $(x/m)_{ads}$ predicted by the fitted model and q_i exp is each value of $(x/m)_{ads}$ measured experimentally, *p* is the number of experiments conducted.

By comparing the results of the values of error function presented in **Table 3.3**, it can be concluded that the Freundlich isotherm model fitted better to the adsorption data for all pesticides. Moreover, Langmuir parameters K_a and Q_{max} for all the soils (except soil 1 for quinalphos and soil 3, soil 4 and soil 5 for congo red) were negative and this could not explain the adsorption process (Bailey and White, 1970). According to the Freundlich isotherms, the K_{fads} value is a relative measurement of the affinity of the adsorbent (soil) for the adsorbate. K_{fads} values ranged from 12.2 to 254.7 for bromophos methyl, from 3.7 to 50.2 for quinalphos, from 1.2 to 28.8 for pretilachlor and from 40.45 to 295.89 for congo red. The highest K_{fads} value for all pesticides corresponds to soil with the highest OM content (soil 1) and this trend is also decreased with decreasing OM content. But for congo red, the highest K_{fads} value corresponds to soil with the lowest OM content (Soil 5) and this trend is also increased with increasing OM content.

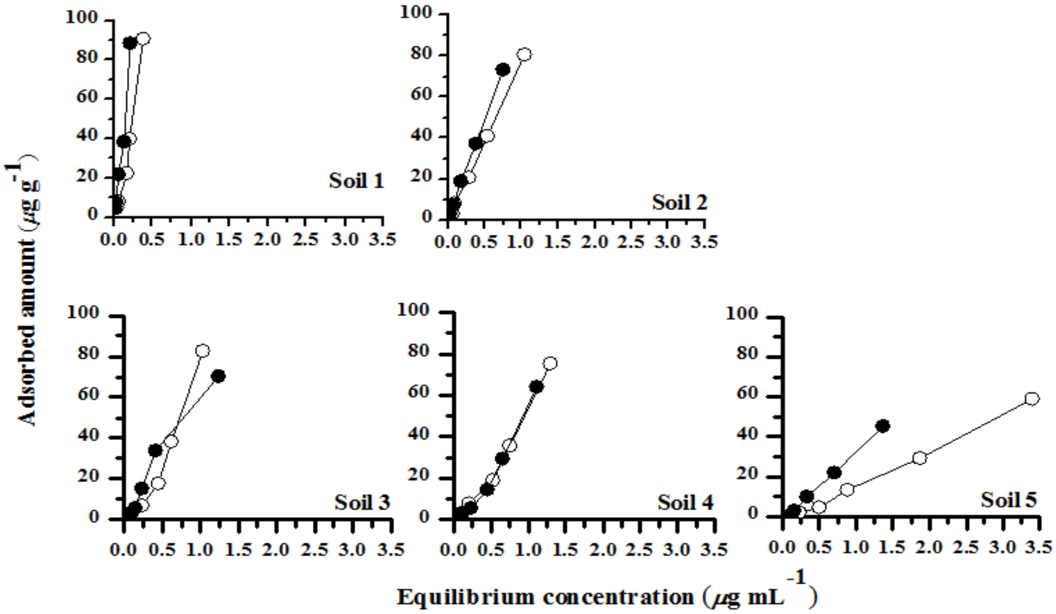


Figure 3.1. Adsorption-desorption isotherms of bromophos methyl on different soils. Open circles (o) indicate adsorption whereas solid circles (•) indicate desorption points

Table 3.3. Freundlich constants (K_{fads}, 1/n) and Langmuir constants (Q_{max}, K_a) values for selected compounds

Compound	Soil	Freundlich constants				Langmuir constants			
		K_{fads}	1/n	R^2	F_{error}	Q_{max}	K_a	R^2	F_{error}
Bromophos methyl	1	254.7(±0.01)	1.23(±0.02)	0.980	0.020	-149.2(±1.2)	-0.84	0.994	0.059
	2	79.4(±0.06)	1.07(±0.10)	0.979	0.056	-41.6(±0.09)	-1.29	0.917	0.527
	3	65.4(±0.04)	1.35(±0.07)	0.967	0.035	-92.6(±0.31)	-0.36	0.987	0.115
	4	49.4(±0.03)	1.20(±0.16)	0.990	0.009	-55.1(±0.25)	-0.53	0.983	0.159
	5	12.2(±0.02)	1.33(±0.04)	0.991	0.007	-20.8(±0.08)	-0.34	0.990	0.857
Quinalphos	1	50.2(±0.08)	0.90(±0.03)	0.956	0.063	37.7(±0.02)	2.53	0.942	0.186
	2	17.1(±0.02)	1.04(±0.07)	0.995	0.011	-55.8(±0.22)	-0.25	0.992	1.034
	3	13.5(±0.04)	1.31(±0.09)	0.941	0.002	-15.7(±0.13)	-0.43	0.789	0.366
	4	11.0(±0.02)	1.03(±0.02)	0.985	0.012	-147.1(±0.21)	-0.06	0.996	0.076
	5	3.7(±0.06)	1.16(±0.08)	0.979	0.014	-23.31(±0.07)	-0.12	0.990	0.158
Pretilachlor	1	28.8(±0.04)	1.7(±0.08)	0.998	0.005	-13.26(±0.02)	-0.69	0.960	0.493
	2	10.4(±0.02)	1.49(±0.02)	0.995	0.021	-12.98(±0.05)	-0.40	0.986	0.645
	3	6.3(±0.02)	1.24(±0.01)	0.996	0.004	-17.60(±0.01)	-0.23	0.986	0.816
	4	4.5(±0.01)	1.06(±0.12)	0.987	0.029	-7.81(±0.11)	-0.31	0.992	0.363
	5	1.2(±0.03)	0.98(±0.07)	0.949	0.061	-1.30(±0.08)	-0.34	0.877	0.502
Congo red	1	40.45(±0.02)	1.26(±0.07)	0.943	0.010	-1428.57(±0.05)	-0.03	0.978	0.023
	2	48.42(±0.06)	1.32(±0.12)	0.994	0.005	-714.29(±0.03)	-0.07	0.994	0.013
	3	164.02(±0.3)	0.56(±0.11)	0.942	0.001	500.00(±0.01)	0.60	0.931	0.038
	4	200.34(±0.02)	0.61(±0.04)	0.934	0.006	526.31(±0.02)	0.73	0.943	0.040
	5	295.89(±0.1)	0.58(±0.05)	0.879	0.000	625.00(±0.06)	1.00	0.933	0.032

[a] *Figure in parentheses is the respective standard error.*

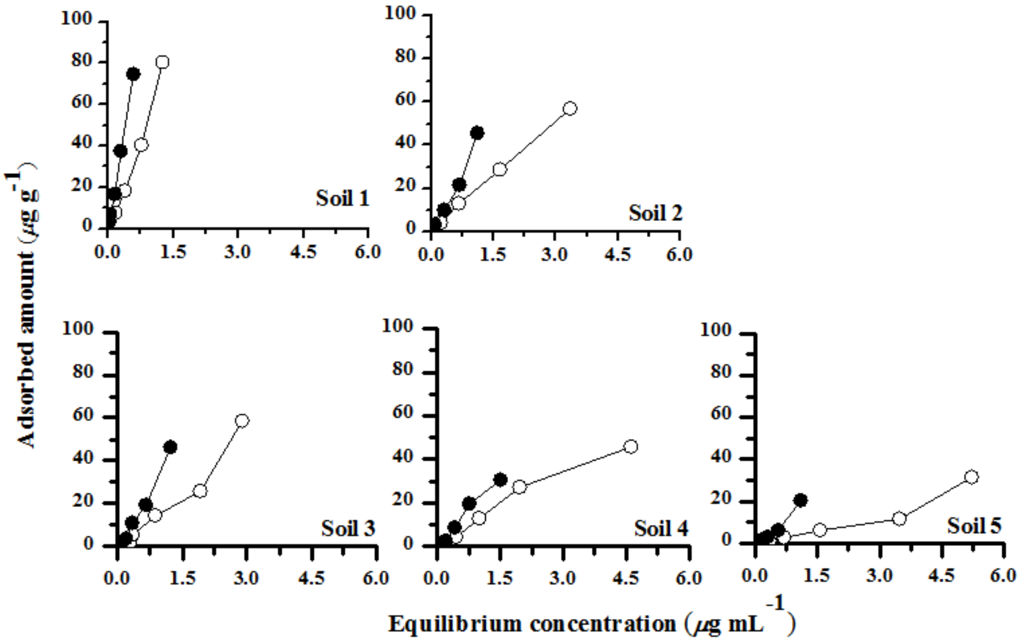


Figure 3.2. Adsorption-desorption isotherms of quinalphos on different soils. Open circles (o) indicate adsorption whereas solid circles (•) indicate desorption points

The $1/n_{ads}$ parameter describes the degree of curvature of the isotherms. The $1/n_{ads}$ values for bromophos methyl **(Table 3.3)** were greater than 1, indicating the S-type of adsorption isotherms (Giles et al., 1974; Giles et al., 1960). This type of isotherm indicates a low affinity between bromophos methyl and soil at low concentration, and the adsorption becomes easier as the pesticide concentration increases. In most cases, this behavior is attributed to the strong competition between the water molecules and the pesticide for the adsorption sites of soil (Calvet, 1989). But in our case, the S-type isotherm may be due to cooperative interactions among adsorbed organic compound that stabilize the sorbate and enhance its affinity for the surface (Limousin et al., 2007). The S-shaped isotherms of organophosphorus pesticides on different adsorbents have also been described by many researchers (Sanchez-Martin and Sanchez-Camazano, 1984; Bowman and Sans, 1977). The $1/n_{ads}$ values for quinalphos **(Table 3)** were also S-type except soil 1 which was near 1 or less than 1, indicating the C-or L-type of adsorption isotherms (Giles et al., 1974; Giles et al., 1960). L-shaped isotherms indicated a relatively high quinalphos and soil affinity at low concentration, and adsorption decreases as the aqueous concentration of pesticides increases. For pretilachlor $1/n_{ads}$ values were higher than 1 for all soils, indicating S-shaped isotherm, whereas in soil 5 showed C or L type isotherm (Figure). Wang et al.(1999) also found the lower $1/n_{ads}$ values for pretilachlor adsorption on low organic matter content soil. The $1/n_{ads}$ values of congo red sorption isotherms for Soil 3, Soil 4 and Soil 5 showed L-shaped isotherms **(Figure 1).** On the other hand, Soil 1 and Soil 2 demonstrated the S-type of adsorption isotherms.

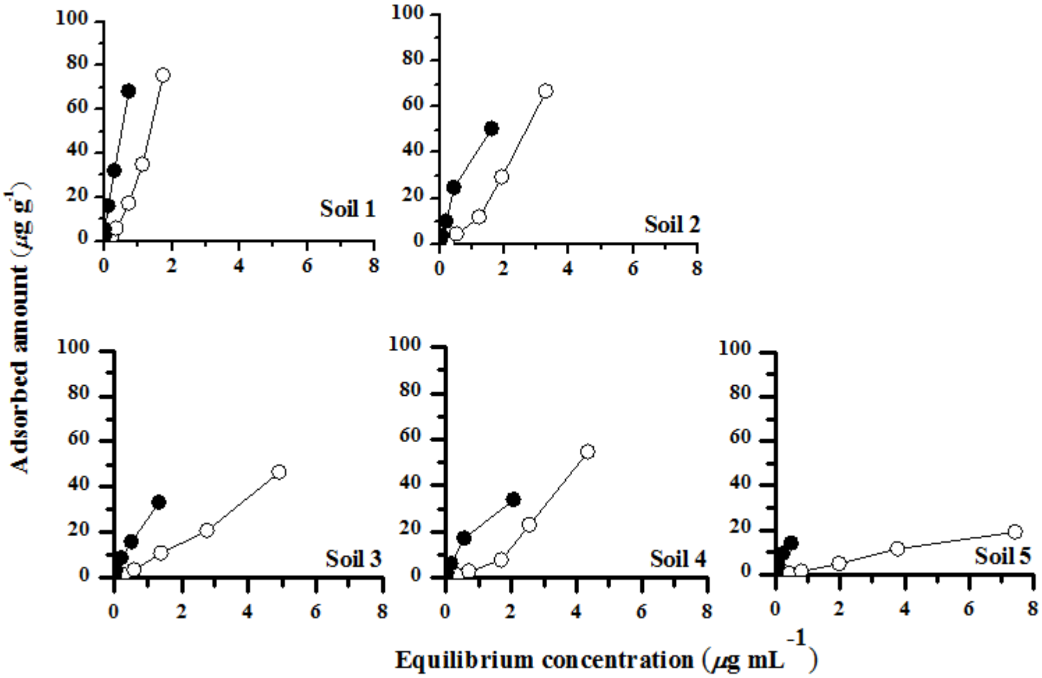


Figure 3.3. Adsorption-desorption isotherms of pretilachlor on different soils. Open circles (o) indicate adsorption whereas solid circles (•) indicate desorption points

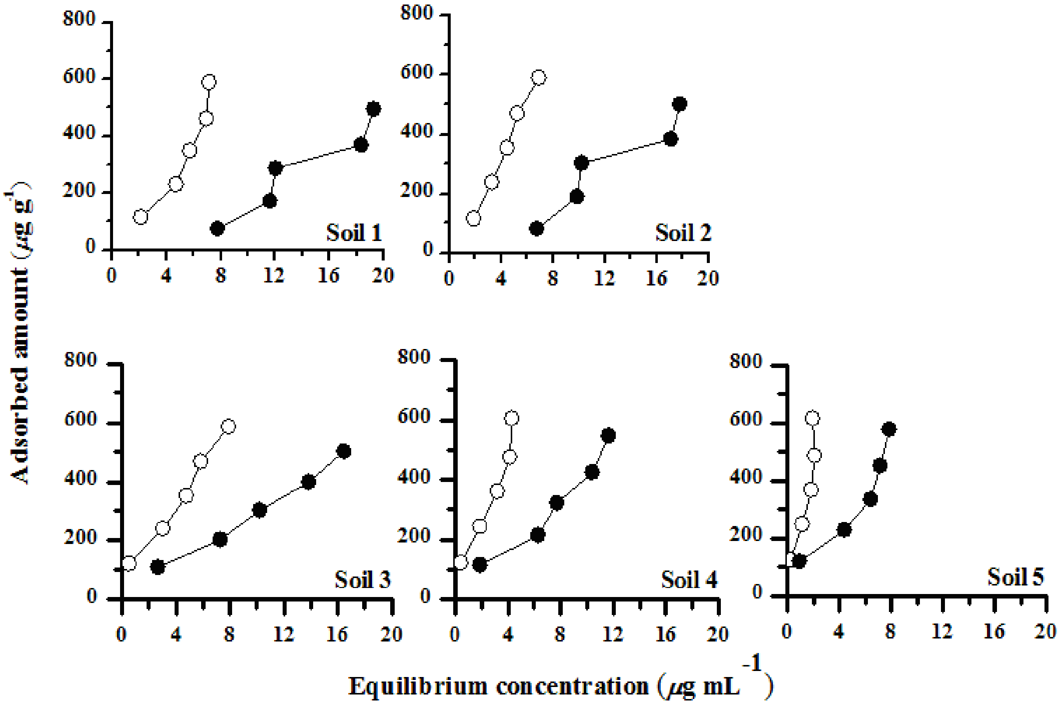


Figure 3.4. Adsorption-desorption isotherms of congo red on different soils. Open circles (o) indicate adsorption whereas solid circles (•) indicate desorption points

Freundlich organic matter distribution coefficient ($K_{f\text{-}om}$) has been presented in **Table 3.4** and the experimental data expressed that $K_{f\text{-}om}$ of soil 1 was higher than that for other four soils studied for all pesticides. A significant positive correlation was observed between Freundlich adsorption capacity (K_{fads}) and $K_{f\text{-}om}$ values. But opposite behaviour was observed for the congo red: a significant negative correlation was found between Freundlich adsorption capacity (K_{fads}) and $K_{f\text{-}om}$ values. Pesticides with $K_{f\text{-}om}$ values below 500 are considered mobile with respect to leaching (Swann et al., 1983). According to this all pesticides and selected dye can be classified as not mobile.

The variation of standard free energy (ΔG^0) values showed that the adsorptivity of the soils was in the order of Soil 1 > Soil 2 > Soil 3 > Soil 4 > Soil 5, and this was also the trend of organic matter content of the soil, indicating adsorption was mostly governed by the organic matter content for all pesticides but congo red showed opposite behaviour, indicating adsorption is mostly governed by the clay content. It is said that greater the ΔG^0 value, higher the extent of adsorption is. ΔG^0 values ranged from -4.42 to -5.0 Kcal/mol for bromophos methyl, from -3.71 to -4.04 Kcal/mol for quinalphos, from -3.05 to -3.71 Kcal/mol for pretilachlor and from -3.91 to -6.31 Kcal/mol for congo red. From

Table 3.4, we can see that all ΔG^0 values were negative showing that adsorption is an exothermic process and an increase in temperature would be expected to reduce adsorption and favor desorption.

Table 3.4. Freudlich $K_{f\text{-}oc}$, $K_{f\text{-}om}$ and thermodynamic parameter ΔG^0 value

Compound	**Soil**	$^*K_{f\text{-}oc}$	$^*K_{f\text{-}om}$	ΔG^0(Kcal/mol)
Bromophos methyl	1	7984.33	4639.34	-5.00
	2	6251.97	3642.20	-4.86
	3	5686.96	3303.03	-4.80
	4	4450.45	2586.39	-4.65
	5	2975.61	1742.86	-4.42
Quinalphos	1	1573.67	914.39	-4.04
	2	1346.46	784.40	-3.95
	3	1173.91	681.82	-3.86
	4	990.99	575.92	-3.76
	5	902.44	528.57	-3.71
Pretilachlor	1	902.82	524.59	-3.71
	2	818.90	477.06	-3.65
	3	547.83	318.18	-3.41
	4	405.41	235.60	-3.23
	5	292.68	171.43	-3.05
Congo red	1	1268.03	736.79	-3.91
	2	3812.60	2221.10	-4.56
	3	14262.61	8283.84	-5.34
	4	18048.65	10489.01	-5.48
	5	72168.29	42270.00	-6.31

$^*K_{f\text{-}om} = 100 \times K_{fads} / OM$, where OM is the soil organic matter content in %

$^*K_{f\text{-}oc} = 100 \times K_{fads} / OC$, where OC is the soil organic carbon content in %

The correlation of adsorption constant K_{fads} with soil properties can be used to predict the adsorption of selected compounds in different soils or to help in determining the factors responsible for adsorption. **Table 3.5** presents the statistical correlations between the K_{fads} values and various soil properties (OM, soil pH and clay). For all pesticides, K_{fads} values were strongly and significantly correlated to the OM content. Data from previous studies also indicate a good correlation between K_{fads} and OM for the organophosphorus pesticides; higher the OM, the larger K_{fads} value is (Sanchez-Martin and Sanchez-Camazano, 1991; Arienzo et al., 1994; Mandal and Adhikari, 1997). On the other hand, clay content was not significantly correlated with Freundlich adsorption values. In addition, adsorption of all pesticides showed very poor correlation with soil pH. This may be attributed to the non-ionisable nature of organophosphorus pesticides. Mandal and Adhikari (1997) also concluded that pH showed very little effect on the adsorption of methyl parathion and fenitrothion in soils. The poor correlation of Freundlich coefficient K_{fads} values with soil pH and clay content also observed by the Wang and coauthors (1999) for pretilachlor adsorption on various soils. Generally, Organic matter in soil is closely associated with the inorganic soil components thus provides a large surface area for adsorption. As a result, adsorption of all pesticides increased with the increase of organic matter content in the soil while no other properties appeared to influence their adsorption behavior. The role of organic matter content for adsorption of similar pesticides has been shown the same behaviour (Hamaker and Thompson, 1972; Rotich, 2004; Braschi et al., 2003).

Correlation coefficient of K_{fads} with soil parameters for selected compounds

Compounds	OM	pH	Clay
Bromophos methyl	0.995*	- 0.331	- 0.755
Quinalphos	0.994*	- 0.318	-0.756
Pretilachlor	0.986*	-0.295	-0.753
Congo red	-0.770	0.301	0.909*

**Significant at 0.05 level (2-tailed).*

But for congo red, there has a significant (Significant at 0.05 level) positive correlation of Freundlich K_{fads} values with soil clay content and adsorption increases with increasing clay content of the soils. Similar, observation was also found by Ketelsen and Meyer-Windel (1999) for sorption of brilliant blue FCF dye on soils. It has been also observed that no other soil properties appeared to be influence the adsorption behavior.

3.4.2 *Desorption isotherms*

Desorption isotherms were constructed using the points resulting from single desorption step measured from all equilibrium points of the adsorption isotherms. Freundlich constants for desorption of bromophos methyl, quinalphos, pretilachlor and congo red are presented in **Table 3.6**. The K_{fdes} was the highest in the Soil 1 and the lowest in the Soil 5 for all pesticides, indicating that soils with high organic matter content have greater affinity for bromophos methyl, quinalphos and pretilachlor than those with lower organic matter content. However, for congo red, The K_{fdes} was the highest in the Soil 5 and the lowest in the Soil 1, indicating that soils with high clay content have greater affinity for congo red than those with lower clay content. As shown in **Table 3.3** and **Table 3.6**, for bromophos methyl, the soil 1, soil 2 and soil 3 have the values $1/n_{ads}$ greater than $1/n_{des}$ This indicates that a significant amount of pesticides adsorbed is not easily desorbed. The opposite behaviour was found for soil 4 and soil 5 and it may happen due to low amount of organic matter. For quinalphos $1/n_{des}$ greater than $1/n_{ads}$, was observed for all soils, indicating that the rate of desorption is higher than the rate of adsorption.

The $1/n_{ads}$ greater than $1/n_{des}$ values were observed for pretilachlor in all soils. For congo red, the values of $1/n_{des}$ is greater than $1/n_{ads}$, indicating that the rate of desorption is higher than the rate of adsorption. According to O'Connor et al. (1980), the ratio of Freundlich exponents, $(1/n_{des}) / (1/n_{ads})$ was assumed to express the hysteresis index (HI). Hysteresis is either not observed when values of HI > 1 and it is evident when HI < 1. In this study, for bromophos methyl, soil 1, soil 2 and soil 3 and for pretilachlor in all soils showed hysteresis. This fact suggests that a fraction of the sorbed bromophos is tightly bound to the soil particles and does not readily desorb. On the other hand soil 4 and soil 5 of bromophos methyl and, quinalphos and congo red in all soils did not show hysteresis indicating soil particles desorbed pesticide molecules easily. For all pesticides the highest hysteresis effect (the lowest HI) was observed in soil 1 which also had the highest organic matter content whereas the lowest hysteresis effect (the highest HI) was observed in the lowest organic matter contained soil. For congo red, the highest hysteresis effect (the lowest HI) was observed in soil 5 which also had the highest clay content, on the other hand, the lowest hysteresis effect (the highest HI) was observed in the lowest clay contained soil.

Table 3.6. Freundlich desorption constants for selected compounds

Compound	Soils	K_{fdes}	1/*n*	R^2	Hysteresis Index(HI)
Bromophos methyl	1	376.2(±0.04)	1.04(±0.02)*	0.984	0.85
	2	93.7(±0.02)	0.95(±0.02)	0.999	0.89
	3	73.0(±0.04)	1.29(±0.06)	0.945	0.96
	4	51.4(±0.02)	1.45(±0.04)	0.993	1.21
	5	36.6(±0.05)	1.66(±0.07)	0.905	1.25
Quinalphos	1	111.1(±0.03)	0.95(±0.12)	0.987	1.06
	2	37.7(±0.09)	1.20(±0.02)	0.985	1.15
	3	39.6(±0.02)	1.58(±0.01)	0.972	1.21
	4	22.0(±0.01)	1.33(±0.08)	0.979	1.29
	5	16.6(±0.02)	1.55(±0.07)	0.989	1.34
Pretilachlor	1	86.5(±0.04)	0.82(±0.08)	0.998	0.48
	2	37.3(±0.03)	0.84(±0.02)	0.989	0.56
	3	27.4(±0.12)	0.78(±0.06)	0.988	0.63
	4	21.5(±0.06)	0.71(±0.01)	0.991	0.67
	5	19.7(±0.09)	0.75(±0.06)	0.938	0.77
Congo red	1	1.80 (±0.09)	1.89(±0.08)	0.913	1.50
	2	4.52(±1.2)	1.63(±0.04)	0.875	1.23
	3	44.26(±.3)	0.83(±0.05)	0.978	1.48
	4	61.56(±0.03)	0.82(±0.02)	0.928	1.34
	5	113.30(±0.04)	0.66(±0.01)	0.876	1.14

**Figure in parentheses is the respective standard error.*

3.4.3. *Adsorption–desorption percent balances*

The mean percent balances for the adsorbed and desorbed amounts of bromophos methyl, quinalphos, pretilachlor and congo red for five different concentrations from different soils are summarized in **Table 3.7**. For all pesticides, it had been observed that adsorption is decreasing with decreasing organic matter content. The highest adsorbed mean percentage was found in Soil 1 for all pesticides which also possessed the highest organic matter content and the lowest for Soil 5 that contained the lowest organic matter content.

A similar result was also reported by Patakioutas and Albanis (2002) for pirimiphos-methyl adsorption on different soils. For congo red, it has been observed that percentage of sorption is increasing with increasing clay content. The highest adsorbed mean percentage was found in Soil 5 (98.10%) which was also possessed high clay content and the lowest was for Soil 1 (92.37%) that contains lowest clay content.

The amount desorbed by the single desorption with 10 ml water ranged from 3.16% to 33.34% for bromophos methyl, from 7.55% to 51.56 % for quinalphos and from 10.7% to 87.0%. Soils containing less organic matter showed greater desorption (Nam et al., 1998) and the pesticides residue moved downward freely through soil column. This observation might cause concern regarding the possibility of ground water contamination, especially from the soil with less organic matter content. The amount of congo red desorbed by the single desorption with 25 ml water ranged from 6.28% to 15.79%. Soils containing less clay content showed greater desorption and potential threat to the environment.

The percentage amounts desorbed in 10 ml acetone ranged from 32.37% to 62.43 % for bromophos methyl, from 17.02% to 36.57% for quinalphos and from 9.7% to20.4% for pretilachlor. High organic matter plays a vital role for binding the pesticide molecules with soil. In case of congo red, the percentage amounts desorbed in 25 ml acetone ranged from 7.12 to 39.22%. For this reason binding molecules were not desorbed with water vigorously from high organic matter content soil or high clay content soil but they did well in organic solvent. The use of organic solvents such as acetone, methanol and acetonitrile, which are very good solvents for many organic compounds, causes considerable desorption and they may break bonds that water may not be able to break.

Finally, the pesticides amounts defined as non-desorbable amount that were relatively high for all analytes, ranged from 4.23% to 64.47% for bromophos methyl, from 11.87% to 75.44% for quinalphos, from 3.3% to 68.9% for pretilachlor and from 44.99 to 86.60% for congo red. The non-desorbable amounts of selected pesticides and dye which dominate in the high organic matter content and high clay content soil respectively are a promising source of contamination in course of time by different weathering processes. Similar observation was also found by Konda et al. (2002). In general, the average percentage of non-desorbed amount of congo red was the highest among the compounds studied. This could be due to the strong bonding between the large molecule of congo red and the soil clay content, that guided lower desorption in water but higher desorption with water. It is also indicating that the congo red is less susceptible for ground water contamination and less bioavailable. The increase in the amounts desorbed by the acetone with increasing soil organic matter indicates that adsorption of pesticides onto organic matter is likely to occur principally via weak induction (London) forces or dispersion forces which are characteristics of the physical adsorption process.

Table 3.7. The percent balances of adsorbed and desorbed amount of selected compounds by the soils

Compound	**Soil**	**%OM**	**Adsorbed %**	***Desorbed in water %**	***Desorbed in acetone %**	***Non-desorbable amount %**
Bromophos methyl	1	5.49	93.9	3.16	32.37	64.47
	2	2.18	87.7	8.79	37.33	53.88
	3	1.98	81.4	17.3	53.25	29.45
	4	1.91	80.2	23.1	58.31	18.59
	5	0.70	54.8	33.34	62.43	4.23
Quinalphos	1	5.49	84.68	7.55	17.02	75.44
	2	2.18	62.6	25.59	22.05	52.36
	3	1.98	56.6	30.54	38.36	31.1
	4	1.91	52.5	37.8	32.02	30.18
	5	0.70	28.0	51.56	36.57	11.87
Pretilachlor	1	5.49	67.6	10.7	20.4	68.9
	2	2.18	51.1	33.7	19.0	47.4
	3	1.98	40.5	49.8	13.5	36.7
	4	1.91	36.5	62.4	11.2	26.4
	5	0.70	16.2	87.0	9.7	3.3
Congo red	1	5.49	92.37	15.79	39.22	44.99
	2	2.18	93.80	13.75	28.37	57.88
	3	1.98	94.70	11.62	30.89	57.49
	4	1.91	96.56	8.80	12.71	78.49
	5	0.70	98.10	6.28	7.12	86.60

**according to the adsorbed amount*

3.5. Conclusion

Adsorption and desorption studies of bromophos methyl, quinalphos, pretilachlor and congo red indicate that selected soils adsorb high amount of these selected compounds. The isotherms fitted to the Freundlich equation well than Langmuir. Soil organic matter content is a major parameter that affects mainly the adsorption behavior of studied pesticides whereas clay content responsible for dye adsorption. Bromophos methyl and congo red showed maximum adsorption and minimum desorption. This suggests that these two compounds is relatively safe pesticide than others. According to the above results, in the natural environment, soils with significant organic matter content and clay content are expected to immobilize these compounds, preventing their movement to the water column.

CHAPTER IV

REMOVAL OF BROMOPHOS METHYL, QUINALPHOS, PRETILACHLOR AND CONGO RED DYE ONTO DIFFERENT ACTIVATED CARBONS BASED ON RESPONSE SURFACE METHODOLOGY

Abstract

In the present work, three pesticides namely, bromophos methyl, quinalphos and pretilachlor, and one hazardous azo dye congo red removal from aqueous solution were investigated using agro-based activated carbons namely, olive seed activated carbon (OSACs), rice husk activated carbon (RHACs) and bagasse activated carbon (BAGACs). The effect of pH, adsorbent dose and concentration on the removal of all compounds by activated carbons (ACs) was investigated using Box Behnken and central composite design based on response surface methodology (RSM) in order to reduce the large number of experiments, time, cost and feasibility. Moreover, the "profiling and desirability function" was used to identify optimum removal% by calculating specific factors optimization simultaneously. The model was evaluated by analysis of variance (ANOVA), lack of fit test (LOF) and finally proposed regression models which fitted the removal data extremely well. After optimization by desirability function, Langmuir and Freundlich adsorption isotherms were developed by using the optimized factors, in order to determine the potential removal capacity of studied activated carbons. The equilibrium data were statistically and satisfactorily fitted to Langmuir isotherms model. Kinetic studies revealed that the removal of all studied compounds was fast by the selected adsorbents with 90% or more of the removal occurring within first 15–20 min of contact time. The kinetic data fits to pseudo second order model well than pseudo first order model.

4.1. Introduction

Adsorption is the most widely used process for the removal of hazardous organic pollutants removal from the contaminated water because of its versatility and feasibility. For these reason, activated carbon is used commercially all over the world for waste water treatments due to its great diversities of surface characteristics. Nevertheless, the available commercial activated carbons are very expensive. So, it is urgently needed for activated carbon production from low cost materials or materials which have no alternative uses and potentially more precise to manufacture.

In this study three activated carbons namely, olive seed activated carbon (OSAC) , rice husk activated carbon (RHAC) and bagasse activated carbon (BAGAC) were chosen in order to removal of three pesticides (bromophos methyl, quinalphos and pretilachlor) and one dye (congo red) from aqueous solutions.

In recent years, several articles had been reported about the removal of pesticides and dye by adsorption onto various activated carbon produced from different raw materials that have been described in section 2.7 (review of literature). But all the previous studies, univariate analyses were adopted for removal that needed more experiments and had lack of interactions of different factors. Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving and optimizing process (Myers and Montgomery, 2002) that is dedicated to the evaluation of relations existing between a group of controlled experimental factors and the observed results of one or more selected criteria.

In this study, removal of selected pesticides from aqueous solutions onto above mentioned activated carbons have been executed from the chemometric point of view based on multivariate response surface methodology (RSM) using Box-Behnken design and for congo red, another approach of design of experiment called Central Composite Design (CCD) design was used. Optimization was performed on the basis of desirability approach in order to find maximum removal percent of selected organic compounds by recalculating of all studied parameters within their ranges, and later isotherm study was carried out by using the optimized factors, in order to determine the removal capacity of used all selected activated carbons.

4.2. Specific objectives of the study

- to determine the kinetic model which suited best to the removal data.

- to removal of selected 3 pesticides and one dye from aqueous solution by selected activated carbon based on response surface methodology.
- to identify the interaction between the parameters and optimization using desirability function.
- to develop isotherm models by using optimized factors obtained from desirability function optimization and
- to determine the adsorption capacity of selected materials in order to remove selected hazardous compounds.

4.3. Materials and methods

4.3.1. *Adsorbents*

The laboratory grade olive seed waste residue activated carbon is used in this present study was collected from the Department of Chemical Engineering, Aristotle University of Thessaloniki, Greece and, rice husk and bagasse activated carbon were collected from the Department of Environmental Engineering, Technical University of Crete, Chania, Greece, The production and characterization of olive seed waste residue, rice husk and bagasse activated carbons have been described elsewhere (Stavropoulos and Zabaniotou, 2005; Kalderis et al., 2008).The obtained activated carbons were used directly as adsorbents without any pretreatments.

4.3.2. *Chemicals*

The pesticides bromophos methyl (99.1% purity), quinalphos (98.9% purity), pretilachlor (99%) were of residue analysis grade and purchased from Riedel-de Haen (Germany) and CR dye was purchased from Riedel-de Haen (Switzerland) and a stock solution of 2000 mg/L of Congo red was prepared. From the stock solution, various concentrations of working solutions were prepared. The physicochemical properties of the selected compounds presented in section 2.5. All other chemicals, solvents and salts were of the highest purity level supplied by Merck pro-analysis or Lab Scan, Pestiscan.

4.3.3. *Characterization*

The important properties of the ACs used in this study are presented in **Table 4.1**.

Table 4.1. Properties of the ACs

Properties	OSACs	RHACs	BAGACs
BET surface area (m^2/g)	1582	811	864
Pore volume (cm^3/g)	1.03	0.41	0.43
Ash content(%)	10.0	27.8	40.6
Average particle size (nm)	-	41.21	54.87

After , Stavropoulos and Zabaniotou (2005); Kalderis et al., (2008).

In order to determine the existence of active functional groups on different activated carbons, FTIR (Fourier Transform Infrared Spectroscopy) spectrometer (Shimadzu -8400, Japan) was used at room temperature with pellet (pressed-disk) technique.

Scanning electron microscopy (SEM) pictures of all activated carbons were taken by Jeol JSM 5600 at 20 kV.

The surface charge (zeta potential) of the activated carbons was measured by Zeta Meter System 3.0 (Zeta-Meter. Inc, USA). The zeta potential was measured 7 times for each pH (3 to 12) and average reading was taken. Between the samples, the cell was flushed with of enough deionised water.

4.3.4. *Experimental procedures*

Batch equilibration method was followed for the optimization process according to the Box-behnken design matrix for all pesticides onto different activated carbons that are presented in **Table 4.2** for bromophos methyl, **Table 4.3** for quinalphos and **Table 4.4** for pretilachlor. For congo red, Central Composite Design (CCD) design matrix that are presented in **Table 4.5** for all activated carbons. For pesticides, 10 ml of pesticides aqueous solution with different pH, initial concentration and adsorbent dose were placed in 15 ml polypropylene centrifuge tube. For congo red, 25 ml of dye solution with different pH, amount of dose and concentrations were placed in 50 ml polypropylene centrifuge tube. The mixture was then shaken at predetermined fixed contact time for specific compounds onto different activated carbons obtained from kinetic study. At the end of the shaking the samples were centrifuged at 4200 rpm for 5 min and the supernatant was collected with a pipette for the determination of compounds concentration.

The removal % was calculated as

$$\text{Removal}\% = 100X\,\frac{(C_0 - C_e)}{C_0} \tag{4.1}$$

where C_0 and C_e are the initial and equilibrium concentrations of specific compounds in the solutions in mg L^{-1} respectively.

4.3.5. *Extraction and analysis of compounds*

For residue analysis of all pesticides, 5 ml of supernatant, each after adsorption and desorption, was extracted twice with 2.5 ml n-hexane using a vortex for 1 min. In the combined extracts a small amount of anhydrous Na_2SO_4 was added to remove residual water. The acetone desorption phase was filtered through glass wool fiber, containing anhydrous Na_2SO_4 as a part of clean up procedure for the samples. An aliquot of 1.0 μL of the *n*-hexane and acetone extract was injected into a Shimadzu 14B gas chromatograph equipped with ^{63}Ni electron capture detector (ECD) at 300^0 C. A DB 1 column (J & W Scientific, Folsom, CA, USA), 30 m of length, 0.32 mm i.d., coated with dimethylpolysiloxane of a film thickness of 0.25 µm was used. The temperature program was: from 80 ^{0}C (2 min) to 290^0 (10 min) at 21^0C min^{-1}. Injector temperature was set to 250 ^{0}C and the injector mode was splitless. Helium and nitrogen was used as the carrier (1.5 mL min^{-1}) and the make-up (35 mL min^{-1}) gases, respectively. Under these conditions, retention times of bromophos methyl, quinalphos and pretilachlor were 11.10, 11.40 and 13.30 minutes respectively. The recovery obtained with the extraction method used was greater than 90% for all pesticides investigated.

Calibration curve of congo red was prepared by measuring absorbance of different predetermined concentrations of the samples at $\lambda_{\max}$ 496 nm using UV–vis spectrophotometer (Jasco, V-530, Japan).

Table 4.2: Box-Behnken design matrix, ranges, levels and results for bromophs methyl removal% onto ACs

	Range and Level		
Factors	Low (-1)	Middle (0)	High (+1)
pH	5	7	9
Adsorbent dose (mg/g)	0.2	0.3	0.4
Initial concentration(mg/L)	1	4	7

Run	pH	Dose	Concentration	Removal %					
				OSACs		*RHACs*		*BAGACs*	
				Observed	Predicted	Observed	Predicted	Observed	Predicted
1	-1	+1	0	99.13	99.13	98.32	97.79	98.03	98.12
2	-1	0	+1	98.00	98.02	96.89	97.26	96.60	96.60
3	0	-1	-1	98.21	98.23	97.50	97.34	97.21	97.30
4	+1	-1	0	97.93	97.93	95.02	95.56	97.73	97.64
5(c)	0	0	0	98.36	98.25	97.55	97.33	97.26	97.21
6	+1	0	-1	98.90	98.88	98.49	98.12	98.20	98.20
7	-1	0	-1	99.47	99.26	98.66	98.73	98.37	98.31
8	-1	-1	0	97.09	97.28	97.31	97.41	97.02	96.99
9	0	-1	+1	97.78	97.57	97.58	97.11	97.29	97.32
10	0	+1	-1	99.43	99.64	99.73	100.20	99.43	99.40
11(c)	0	0	0	98.22	98.25	97.31	97.33	97.22	97.21
12	+1	0	+1	97.95	98.16	96.74	96.68	97.45	97.51
13	+1	+1	0	98.44	98.25	98.53	98.44	98.24	98.27
14(c)	0	0	0	98.17	98.25	97.11	97.33	97.14	97.21
15	0	+1	+1	98.36	98.34	97.35	97.51	97.06	96.98

Note: (c) indicates central point

Table 4.3: Box-Behnken design matrix, ranges, levels and results for quinalphos removal% onto ACs

	Range and Level		
Factors	Low (-1)	Middle (0)	High (+1)
pH	5	7	9
Adsorbent dose (mg/g)	0.2	0.3	0.4
Initial concentration(mg/L)	1	4	7

Run	pH	Dose	Concentration	Removal %					
				OSACs		*RHACs*		*BAGACs*	
				Observed	Predicted	Observed	Predicted	Observed	Predicted
1	-1	+1	0	98.14	98.14	97.26	97.36	98.46	98.24
2	-1	0	+1	97.02	97.16	95.76	95.76	95.95	96.14
3	0	-1	-1	97.23	97.38	95.97	96.06	96.16	96.13
4	+1	-1	0	96.95	96.95	95.69	95.60	95.88	96.10
5(c)	0	0	0	97.88	97.80	96.47	96.29	96.76	96.55
6	+1	0	-1	97.91	97.77	96.64	96.64	96.83	96.64
7	-1	0	-1	98.48	98.40	97.20	97.35	97.40	97.61
8	-1	-1	0	96.12	96.06	94.87	94.62	95.06	94.88
9	0	-1	+1	96.80	96.72	95.54	95.79	95.74	95.73
10	0	+1	-1	98.44	98.52	98.66	98.42	98.36	98.36
11(c)	0	0	0	97.74	97.80	96.27	96.29	96.66	96.55
12	+1	0	+1	96.97	97.06	95.71	95.56	95.90	95.69
13	+1	+1	0	96.46	96.52	95.21	95.46	95.40	95.58
14(c)	0	0	0	97.79	97.80	96.12	96.29	96.21	96.55
15	0	+1	+1	97.38	97.23	96.12	96.02	96.31	96.34

Note: (c) indicates central point

Table 4.4: Box-Behnken design matrix, ranges, levels and results for pretilachlor removal% onto ACs

	Range and Level		
Factors	Low (-1)	Middle (0)	High (+1)
pH	5	7	9
Adsorbent dose (mg/g)	0.2	0.3	0.4
Initial concentration(mg/L)	1	4	7

Run	pH	Dose	Concentration	Removal %					
				OSACs		*RHACs*		*BAGACs*	
				Observed	Predicted	Observed	Predicted	Observed	Predicted
1	-1	+1	0	96.68	96.68	97.16	97.16	97.78	97.41
2	-1	0	+1	95.56	95.64	96.04	96.12	94.67	94.87
3	0	-1	-1	95.77	95.85	96.25	96.33	94.88	94.71
4	+1	-1	0	95.51	95.51	95.99	95.98	94.62	94.99
5(c)	0	0	0	96.16	96.07	96.64	96.55	95.33	95.19
6	+1	0	-1	96.44	96.36	96.92	96.84	95.54	95.34
7	-1	0	-1	97.00	96.86	97.48	97.34	96.10	96.33
8	-1	-1	0	94.68	94.74	95.15	95.21	93.80	93.74
9	0	-1	+1	95.35	95.21	95.82	95.68	94.46	94.32
10	0	+1	-1	96.96	97.10	97.44	97.59	97.06	97.20
11(c)	0	0	0	96.03	96.07	96.51	96.55	95.04	95.19
12	+1	0	+1	95.52	95.67	96.00	96.14	94.63	94.40
13	+1	+1	0	95.51	95.45	95.99	95.92	94.62	94.68
14(c)	0	0	0	96.03	96.07	96.51	96.55	95.20	95.19
15	0	+1	+1	95.92	95.84	96.40	96.31	95.03	95.20

Note: (c) indicates central point

Table 4.5. Central composite design(CCD) matrix for congo red removal onto different activated carbons

	Range and Level				
Factors	*-α*	*-1(Low)*	*0 (Middle)*	*+1(High)*	*+α*
pH	2.64	4	6	8	9.36
Dose (g)	0.13	0.20	0.30	0.40	0.47
Concentration (mg L^{-1})	7.96	25	50	75	92.04

Run	*pH*	*Dose*	*Concentration*	*Removal %*					
				OSACs		*RHACs*		*BAGACs*	
				Observed	*predicted*	*Observed*	*predicted*	*Observed*	*predicted*
1	+1	+1	-1	95.90	97.92	91.42	93.88	94.89	89.64
2	+1	-1	+1	84.68	84.92	72.77	71.44	82.68	78.20
3(c)	0	0	0	96.36	96.12	92.05	93.77	96.66	94.59
4	0	-α	0	82.01	84.49	64.12	68.90	88.57	87.57
5	0	0	+α	96.64	96.34	89.55	90.04	67.89	71.28
6	-1	-1	+1	96.64	94.57	80.72	77.73	63.64	66.55
7	-1	+1	+1	99.40	101.20	98.00	98.26	96.96	93.25
8(c)	0	0	0	94.86	96.12	95.04	93.77	94.22	94.59
9	+1	-1	-1	92.29	90.45	84.05	83.25	95.74	97.10
10	0	0	-α	98.48	98.84	97.00	97.27	94.06	93.98
11	-1	+1	-1	98.92	98.64	94.26	95.05	99.21	101.35
12	+α	0	0	90.36	89.80	85.97	83.84	87.04	92.26
13	0	+α	0	98.76	96.34	99.11	95.09	99.45	103.76
14	+1	+1	+1	91.59	92.08	89.82	92.63	97.03	94.71
15(c)	0	0	0	97.16	96.12	94.36	93.77	93.47	94.59
16	-α	0	0	97.89	98.51	87.23	90.12	94.22	92.31
17	-1	-1	-1	92.22	91.69	88.44	85.09	98.62	98.60

Note: (c) indicates central point

4.4. Results and discussion

4.4.1. *FTIR analyses of adsorbents*

4.4.1.1. Olive seed ACs.

The FTIR spectrum of the olive seed waste residue activated carbon is shown in **Figure 4.1**. The medium band located at 515-690 cm^{-1} revealed the alkyl halides (C-Br stretch). The 910-950 cm^{-1} absorption band corresponded to O-H bend of carboxylic acids. The sharp peak of C-O stretch at 1000-1320 cm^{-1} also indicated the existence of alcohols, carboxylic acids, esters and ethers functional groups. The bands at 1350-1550 cm^{-1} is represented the C–H bend of alkanes, N–O asymmetric stretch of nitro compounds. The vibrations at 2200-2300 cm^{-1} is stated the C≡N stretch of nitriles compound. The strong and very broad band of O–H stretch of carboxylic acids also observed at 2400-3300 cm^{-1}. The band at 3300-3600 cm^{-1} attributed to hydrogen bonded O-H stretch of alcohols, phenols.

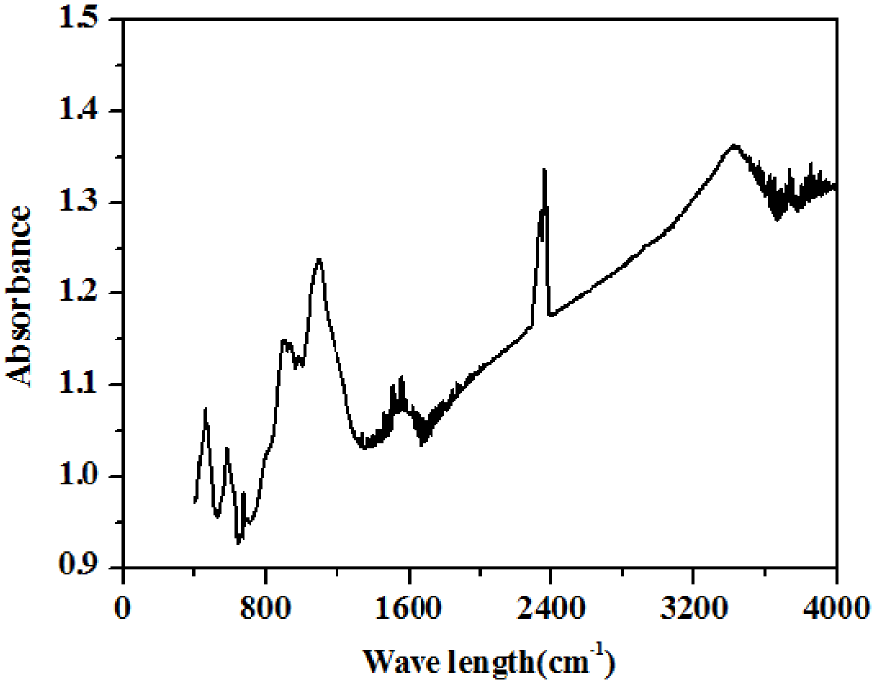


Figure 4.1. FTIR- spectra of olive seed activated carbons

4.4.1.2. Rice husk activated carbons

The FTIR approach is an important tool for identifying some characteristic functional groups, which can adsorb compound ions from the solutions. Most of the activated carbon contains some oxygen complexes on the surface, i.e. (a) strongly carboxylic groups, (b) carbonyl groups and (c) phenolic groups (Motoyuki, 1990). Like FTIR analysis of OSACs rice husk yielded medium peaks at about 910 cm^{-1} and strong peak at 1384 cm^{-1} which are assigned to the carboxylic groups; the peak at 3300 cm^{-1} is also associated with the carboxylic groups.

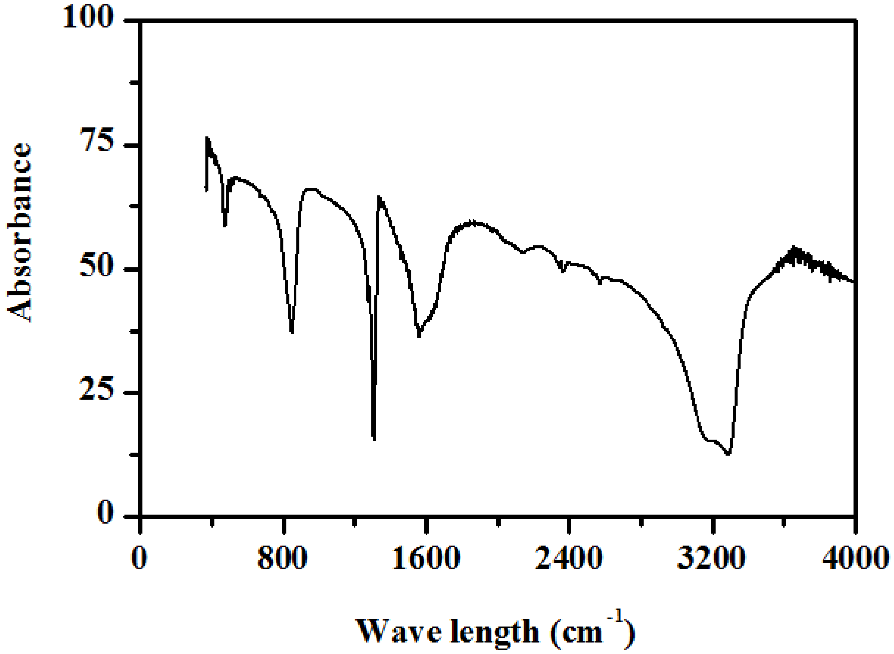


Figure 4.2. FTIR- spectra of rice husk activated carbons

4.4.1.3. Bagasse activated carbons

Like OSACs and RHACs, bagasse activated carbons also showed the same functional groups on its surface. More general, the IR spectrum of the activated adsorbents showed weak and broad peaks in the range of 3853–500 cm-1. Approximate FT-IR band assignment indicated the presence of carbonyls, carboxyls, lactones, phenols, olefinic and aromatic structures. Abroad peak at 3250-3500 responsible for alcohol group, whereas a sharp peak at 1000-1100 cm^{-1} attributed to carboxylic (C-O stretch) groups.

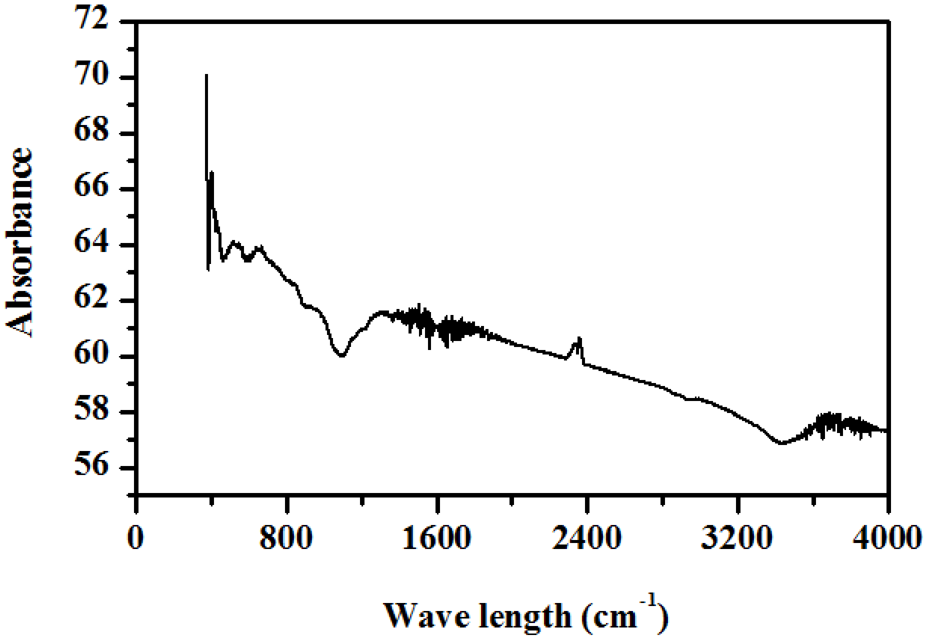


Figure 4.3. FTIR- spectra of bagasse activated carbons

4.4.2. *SEM analyses of adsorbent*

The Scanning electron microscopy (SEM) pictures for OSACc (Figure 4.4), RHACs (Figure 4.5), and BAGACs (Figure 4.6) showed porous and homogeneous surface that was enough responsible for selected compounds adsorption.

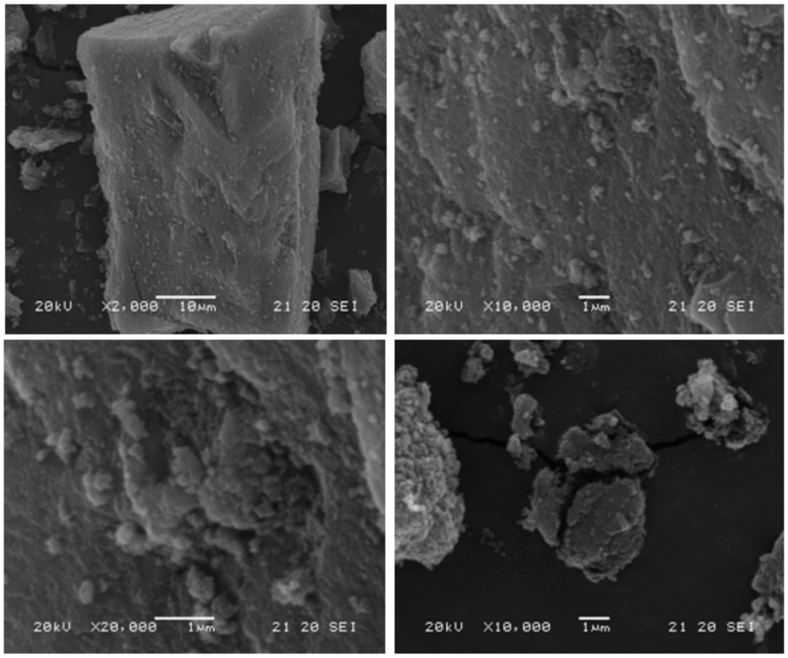


Figure 4.4. SEM pictures of olive waste residue activated carbons

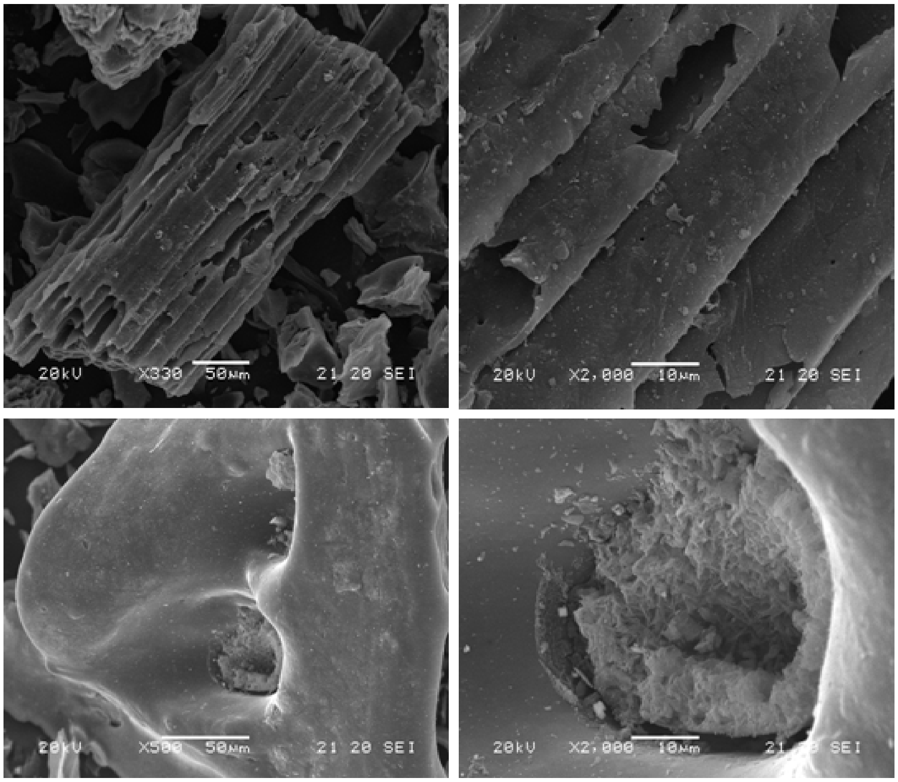


Figure 4.5. SEM pictures of rice husk activated carbons

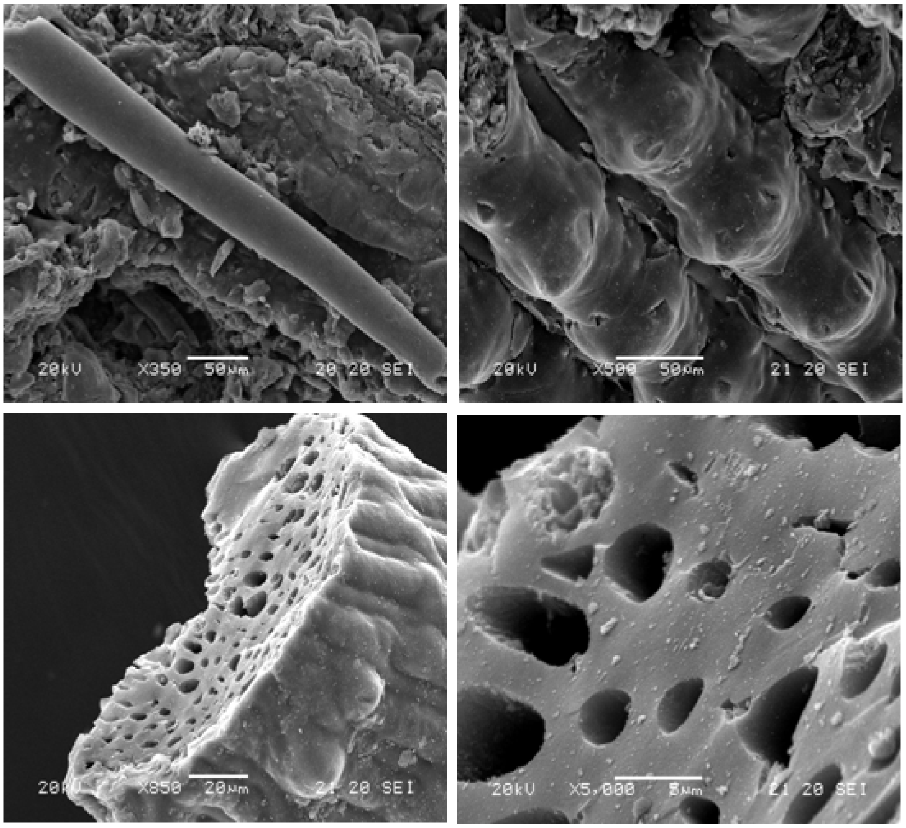


Figure 4.6. SEM pictures of bagasse activated carbons

4.4.3. *Effect of contact time*

From **Figure 4.7**, it may be seen that the percentage adsorption for all compounds increases with an increase in the contact time and attains equilibrium after some time. For instances, it has been seen from the **Figure 4.7** that congo red attained its equilibrium point more faster (within 90 minutes,) than other pesticides studied (within 150 minutes). The quicker attainment of equilibrium point for CR may be possible due to the higher surface area OSACs than other ACs. After this equilibrium points, no more removal percentage was observed for all compounds. From the above observation, it is evident that with the increases contact time, the external mass transfer coefficient increases resulting in quicker adsorption of the CR dye molecules.

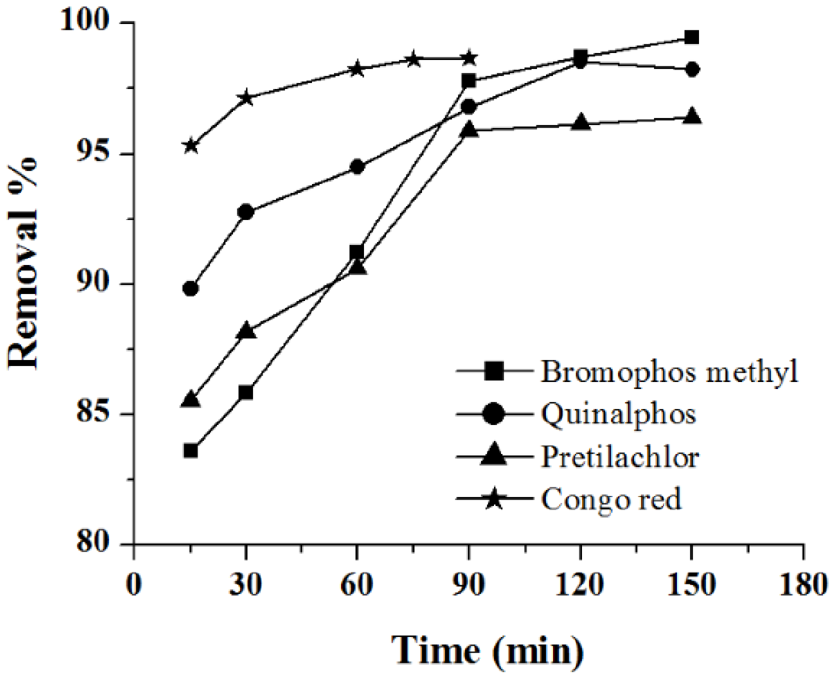


Figure 4.7. Effect of contact time for the removal of bromophos methyl, quinalphos, pretilachlor and congo red onto OSACs (ACs dosage = 0.3g/10ml in Deionised (DI) water, Concentration = 10 mg/l, for pesticides and AC dosage= 0.3 g/25ml in DI water, Concentration =50 mg/L for congo red

Figure. 4.8 indicate the effect of contact time on percentage removal of selected compounds removed onto RHACs. The percentage of removal is observed to increase with increasing contact time. For the first 15 min contact time, 0.3 g of activated carbons removed more than 87% compounds from the solutions and it gradually increased with increasing contact time and finally adsorbed more than 98% for all pesticides at 150 min and reached the equilibrium. But congo red has taken more time (about 300 min) in order to reached its equilibrium. The surface area of RHACs is lower than other ACs studied, for this reason large molecule of CR was adsorbed more slowly than other pesticides compounds.

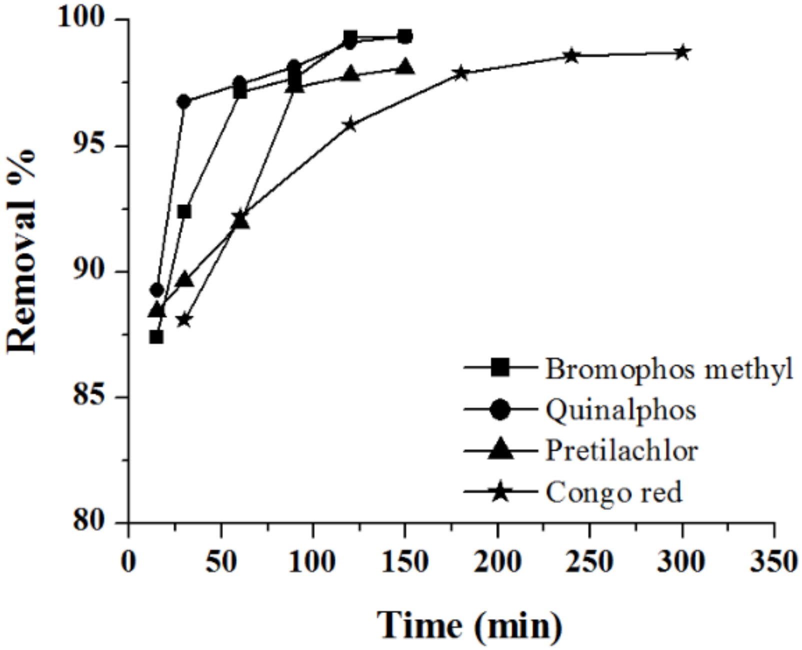


Figure 4.8. Effect of contact time for the removal of bromophos methyl, quinalphos, pretilachlor and congo red onto RHACs (ACs dosage = 0.3g/10ml in DI water, Concentration = 10 mg/l, for pesticides and AC dosage= 0.3 g/25ml in DI water, Concentration =50 mg/L for congo red

The influence of contact time for the removal of different selected compounds onto BAGACs is presented in Figure 4.9. The removal increased 86.32–98.90%, 85.96–98.59%, 85.54–96.38% and 81.12–97.43% for bromophos methyl, quinalphos, pretilachlor and congo red with an increase in contact time (15–150 min, 30-180 min for CR) and became almost constant after 150 min for pesticides and 180 min for CR. The equilibration time of 150 min for pesticides and 180 min for CR was selected for further studies.

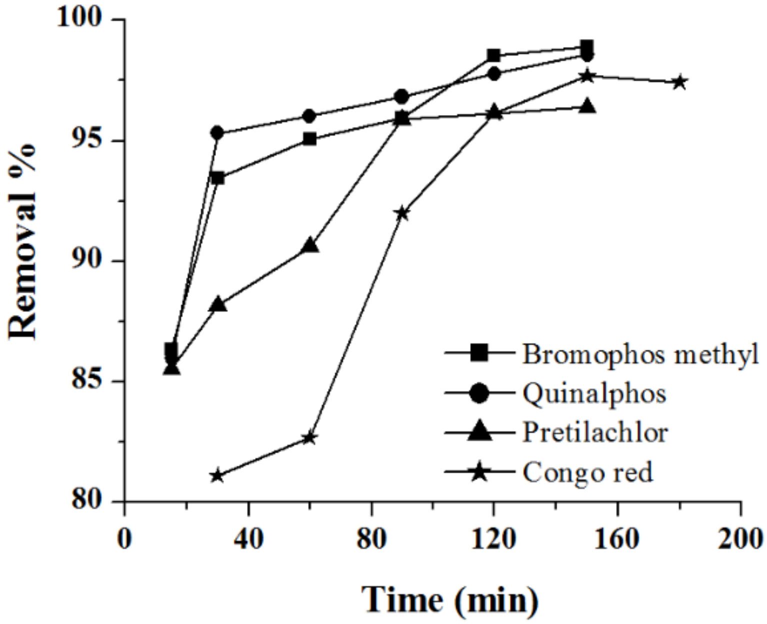


Figure 4.9. Effect of contact time for the removal of bromophos methyl, quinalphos, pretilachlor and congo red onto BAGACs (ACs dosage = 0.3g/10ml in DI water, Concentration = 10 mg/l, for pesticides and AC dosage= 0.3 g/25ml in DI water, Concentration =50 mg/L for congo red

4.4.4. *Kinetic study*

Two widely used kinetic models were applied in this study in order to analyze kinetic data. The parameters were the same as mentioned earlier for effect of contact time study. Lagergren pseudo first order model can be represented by following the equation (4.2)

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1 t}{2.303} \tag{4.2}$$

The pseudo second order can be expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^{\,2}} + \frac{1}{q_e} t \tag{4.3}$$

where q_e the amount of compounds adsorbed onto ACs at equilibrium (mg g^{-1}) and q_t is the amount (mg g^{-1}) of compounds adsorbed at any time t (min) and K_1 and K_2 are the rate constants of pseudo first order and second order model respectively.

Table 4.6. A comparison of the pseudo first order rate constants and pseudo second order rate constant with calculated (q_e-cal) and experimental (q_e-exp) values obtained at single initial concentration.

ACs. Type	Compounds	q_e, exp	Kinetic model					
			Pseudo-first order			Pseudo-second order		
			K_1	q_e, cal.	R^2	K_2	q_e, cal.	R^2
OSACs	Bromophos methyl	0.182	0.031	0.987	0.954	1.015	0.188	0.999
	Quinalphos	0.226	-0.034	0.082	0.511	1.866	0.229	0.999
	Pretilachlor	0.267	0.039	0.324	0.919	1.123	0.272	0.999
	Congo red	4.116	0.058	0.957	0.954	0.356	4.147	1.000
BAGACs	Bromophos methyl	0.305	0.028	0.286	0.866	1.147	0.309	0.999
	Quinalphos	0.281	-0.014	0.108	0.114	1.653	0.284	0.999
	Pretilachlor	0.267	0.039	0.324	0.919	1.106	0.272	0.999
	Congo red	4.210	-0.002	0.641	0.006	0.020	4.49	0.998
RHACs	Bromophos methyl	0.307	0.044	0.353	0.881	1.229	0.311	0.999
	Quinalphos	0.306	0.031	0.234	0.901	2.055	0.309	0.999
	Pretilachlor	0.297	0.035	0.220	0.918	1.009	0.304	0.999
	Congo red	4.386	0.020	1.009	0.976	0.046	4.46	1.000

The two models were developed by constructing linear plot of log ($q_e - q_t$) vs. t for pseudo first order and t/q_t vs. t for pseudo second order model. The rate constants K_1, K_2 measured from the slopes of corresponding linear plots. According to the regression coefficient, the adsorption of all selected compounds onto different ACs is best described by the pseudo second order kinetic model than pseudo first order **(Table 5.6)**. Besides, the calculated q_e values for pseudo second order kinetic model is similar to experimental q_e values indicating the best fitted model **(Figure 4.10, 4.11, 4.12)** than pseudo first order model. Similar results were also reported by mall and coauthors (2005) for congo red removal by fly ash and activated carbon, and imidaclopride removal from aqueous solution by adsorption onto granular activated carbon (Daneshvar et al., 2007).

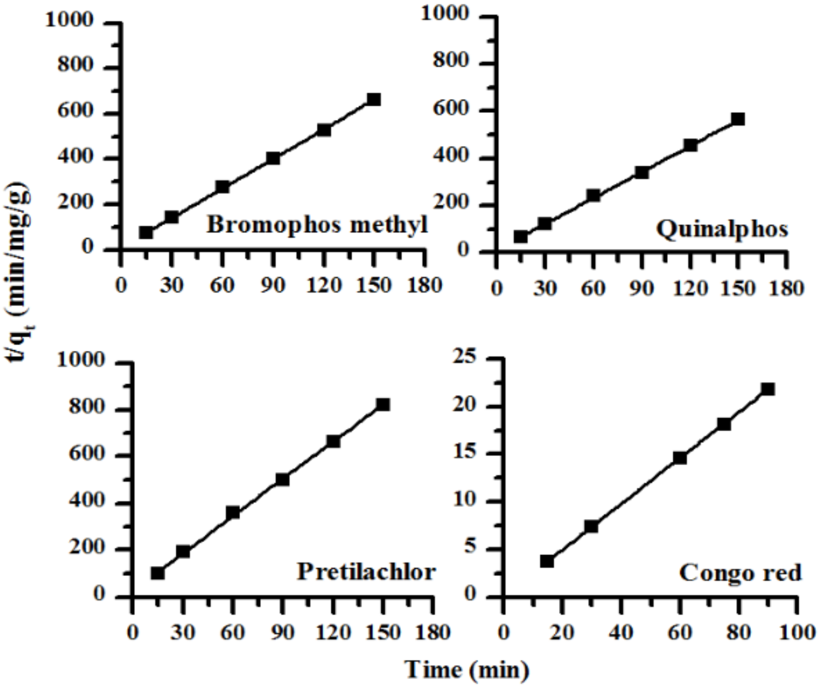


Figure 4.10. Pseudo second order kinetic plot for OSACs, where ACs dosage = 0.3g/10ml in DI water, Concentration = 10 mg/l, for pesticides and ACs dosage= 0.3 g/25ml in DI water, Concentration =50 mg/L for congo red

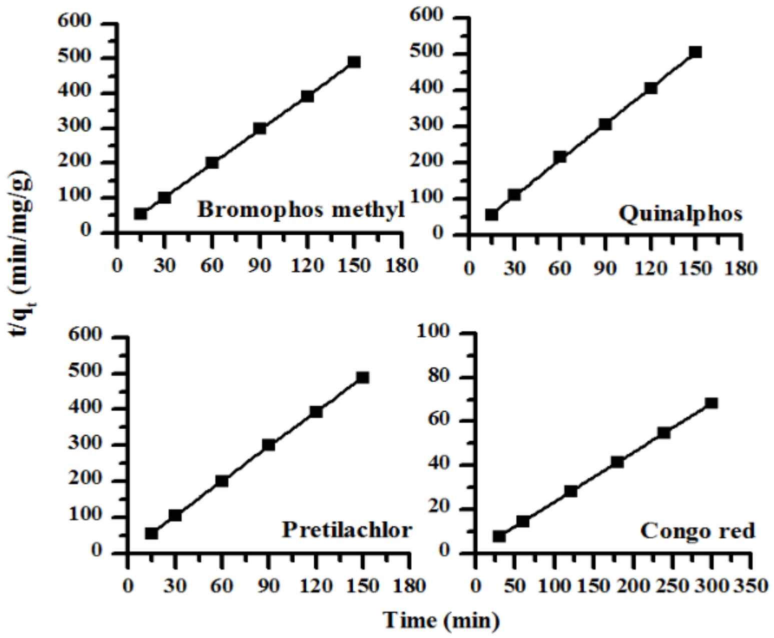


Figure 4.11. Pseudo second order kinetic plot for RHACs, where ACs dosage = 0.3g/10ml in DI water, Concentration = 10 mg/l, for pesticides and ACs dosage= 0.3 g/25ml in DI water, Concentration =50 mg/L for congo red

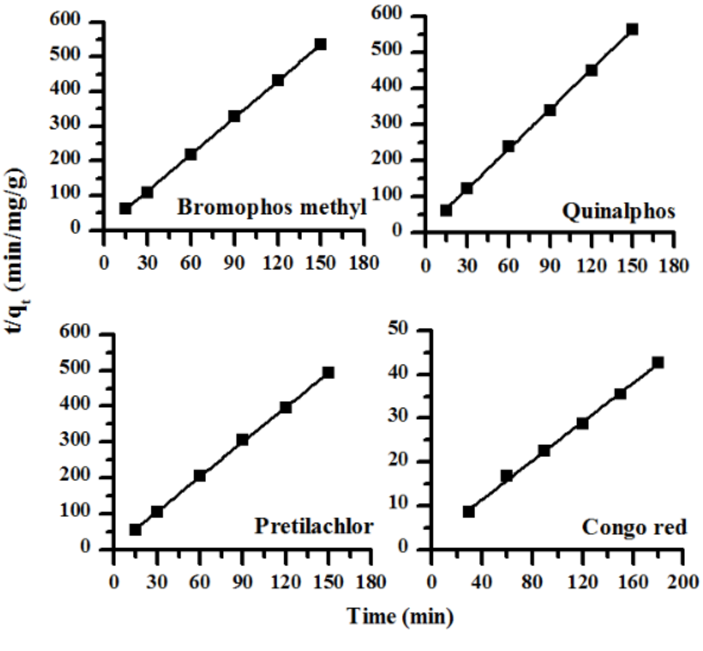


Figure 4.12. Pseudo second order kinetic plot for BAGACs, where ACs dosage = 0.3g/10ml in DI water, Concentration = 10 mg/l, for pesticides and ACs dosage= 0.3 g/25ml in DI water, Concentration =50 mg/L for congo red

4.4.5. *Statistical analysis based on response surface methodology*

Box-Behnken is an efficient three-level design for fitting second-order response surfaces. The most important advantage of Box-Behnken design is that it does not contain combinations for which all factors are at the same time at their highest or lowest levels and in particular it avoids treatment combinations that are extreme (Ferreira et al., 2007). The pH, initial concentration and adsorbent dose are the vital parameters which effect adsorption process. **Table 4.2** (for bromophos methyl), **Table 4.3** (for quinalphos) and **Table 4.4** (for pretilachlor), represents the experimental parameters and levels used by Box-Behnken design model for OSACs, RHACs and BAGACs respectively. The corresponding design matrix consisted of 15 experiments including three center points.

Congo red is a dipolar molecule and it shows different behaviour at different pH. Moreover CR has very high molecular weight (696.67). Therefore, it needed wide range of pH and concentration study, but Box-Behnken design is restricted only three level design and couldn't capable of handling more than three levels of factors. Under these circumstances, another powerful statistical design that is central composite design (CCD) based on RSM is used for handling the data of CR. The CCD is an efficient design that is ideal for sequential experimentation and allows a rational amount of information for testing lack of fit while not involving an unusually large number of design points (Myers and Montgomery, 2002). The central composite design (CCD) is the most successfully employed RSM technology for removal hazardous compounds that was used by different researchers (Arenas et al., 2007; Garg et al., 2008; Tan et al., 2008). For congo red, Central Composite Design (CCD) design matrix are presented in **Table 4.5** for all activated carbons. In the present study, the three factors CCD with two levels experimental (2^3) design model, containing 8 factorial points, 6 axial points and 3 replicates at the center points were employed, indicating that altogether 17 experiments were required (($N=2^n+2n+n_c=2^3+2*3+3=17$), where N is the total number of experiments required, n is the number of factors and n_c is the center points). The center points are used to determine the experimental error and the replication of the data. The pH, adsorbent dose and initial concentration were the input factors in order to get the highest removal % of CR onto different selected activated carbons. In this study, α value was fixed at 1.682 (rotatable).

STATISTICA® statistical software was used for the design of experiment. A second order polynomial model used to fit the response to the independent variables is shown:

$$y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \qquad (4.4)$$

where y is the percentage of compounds removal, β_0 the intercept and $\beta_{i,}$ $\beta_{ii},$ β_{ij} are the coefficients of parameters for linear, squared and interaction factor effects respectively.

Generally, it has been established that lots of factor regulating the adsorption process; among them adsorbent physical and chemical properties (porous structure, surface chemistry etc.), adsorbate (solubility, polarity, functional groups, etc.) and conditions of the process (pH, temperature, mixing, batch or dynamic process, concentration of adsorbate, grain size and dose of adsorbent and others). However, it is quite difficult to consider all parameters during the adsorption experiments because of multitude of experiments and intricate data analysis. Therefore, the pH, initial concentration and adsorbent dose are the vital parameters which effect adsorption process selected according to literature survey. In order to evaluate the combined effects of these factors, experiments were executed with the combinations of different parameters using Box-Behnken and CCD design.

Table 4.7. ANOVA for Response Surface Quadratic Model for bromophos methyl, quinalphos and pretilachlor onto olive seed activated carbon

Bromophos methyl

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	0.029	2	0.014	1.474	0.404
(2)Dose(L+Q)	2.417	2	1.209	124.607	0.008
(3)Initial concentration(L+Q)	2.284	2	1.142	117.746	0.008
1*2	0.585	1	0.585	60.333	0.016
1*3	0.068	1	0.068	6.969	0.119
2*3	0.102	1	0.102	10.557	0.083
Lack of Fit	0.250	3	0.083	8.599	0.106
Pure Error	0.019	2	0.010		
Correction Total	5.778	14			

R^2=0.953; Adjusted R^2=0.869; L indicated linear effect; Q indicated quadratic effect

Quinalphos

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	0.794	2	0.397	78.871	0.013
(2)Dose(L+Q)	2.335	2	1.168	231.957	0.004
(3)Initial concentration(L+Q)	1.996	2	0.998	198.292	0.005
1*2	1.575	1	1.575	312.919	0.003
1*3	0.068	1	0.068	13.430	0.067
2*3	0.099	1	0.099	19.714	0.047
Lack of Fit	0.119	3	0.040	7.853	0.115
Pure Error	0.010	2	0.005		
Correction Total	6.990	14			

R^2=0.982; Adjusted R^2=0.948; L indicated linear effect; Q indicated quadratic effect

Pretilachlor

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	0.222	2	0.111	19.744	0.048
(2)Dose(L+Q)	2.109	2	1.054	187.172	0.005
(3)Initial concentration(L+Q)	2.021	2	1.010	179.360	0.006
1*2	1.000	1	1.000	177.515	0.006
1*3	0.068	1	0.068	12.000	0.074
2*3	0.096	1	0.096	17.059	0.054
Lack of Fit	0.117	3	0.039	6.917	0.129
Pure Error	0.011	2	0.006		
Correction Total	5.682	14			

R^2=0.977; Adjusted R^2=0.937; L indicated linear effect; Q indicated quadratic effect

Table 4.8. ANOVA for Response Surface Quadratic Model for bromophos methyl, quinalphos and pretilachlor onto rice husk activated carbon

Bromophos methyl					
Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	0.84	2	0.42	8.67	0.10
(2)Dose(L+Q)	5.40	2	2.70	55.48	0.02
(3)Initial concentration(L+Q)	5.38	2	2.69	55.28	0.02
1*2	1.56	1	1.56	32.07	0.03
1*3	0.00	1	0.00	0.00	0.96
2*3	1.51	1	1.51	30.95	0.03
Lack of Fit	1.38	3	0.46	9.42	0.10
Pure Error	0.10	2	0.05		
Correction Total	16.21	14			

R^2=0.909; Adjusted R^2=0.745; L indicated linear effect; Q indicated quadratic effect

Quinalphos					
Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	0.98	2	0.49	16.05	0.06
(2)Dose(L+Q)	3.42	2	1.71	56.12	0.02
(3)Initial concentration(L+Q)	4.23	2	2.12	69.51	0.01
1*2	2.07	1	2.07	67.83	0.01
1*3	0.07	1	0.07	2.16	0.28
2*3	1.12	1	1.12	36.88	0.03
Lack of Fit	0.32	3	0.11	3.55	0.23
Pure Error	0.06	2	0.03		
Correction Total	12.38	14			

R^2=0.969; Adjusted R^2=0.913; L indicated linear effect; Q indicated quadratic effect

Pretilachlor					
Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	0.22	2	0.11	19.74	0.05
(2)Dose(L+Q)	2.13	2	1.06	187.17	0.01
(3)Initial concentration(L+Q)	2.04	2	1.02	179.36	0.01
1*2	1.01	1	1.01	177.51	0.01
1*3	0.07	1	0.07	12.00	0.07
2*3	0.10	1	0.10	17.06	0.05
Lack of Fit	0.12	3	0.04	6.92	0.13
Pure Error	0.01	2	0.01		
Correction Total	5.74	14			

R^2=0.977; Adjusted R^2=0.937; L indicated linear effect; Q indicated quadratic effect

Table 4.9. ANOVA for Response Surface Quadratic Model for bromophos methyl, quinalphos and pretilachlor onto bagasse activated carbon

Bromophos methyl

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	0.51	2	0.26	68.04	0.01
(2)Dose(L+Q)	1.92	2	0.96	255.08	0.00
(3)Initial concentration(L+Q)	3.07	2	1.53	408.22	0.00
1*2	0.06	1	0.06	16.61	0.06
1*3	0.26	1	0.26	69.14	0.01
2*3	1.50	1	1.50	398.88	0.00
Lack of Fit	0.04	3	0.01	3.67	0.22
Pure Error	0.01	2	0.014		
Correction Total	7.27	14			

R^2=0.993; Adjusted R^2=0.981; L indicated linear effect; Q indicated quadratic effect

Quinalphos

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	1.22	2	0.61	7.11	0.12
(2)Dose(L+Q)	4.09	2	2.04	23.84	0.04
(3)Initial concentration(L+Q)	3.09	2	1.55	18.06	0.05
1*2	3.77	1	3.77	43.98	0.02
1*3	0.07	1	0.07	0.77	0.47
2*3	0.66	1	0.66	7.69	0.11
Lack of Fit	0.33	3	0.11	1.30	0.46
Pure Error	0.17	2	0.09		
Correction Total	13.43	14			

R^2=0.962; Adjusted R^2=0.894; L indicated linear effect; Q indicated quadratic effect

Pretilachlor

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	1.08	2	0.54	24.88	0.04
(2)Dose(L+Q)	5.67	2	2.84	130.18	0.01
(3)Initial concentration(L+Q)	2.90	2	1.45	66.52	0.01
1*2	3.96	1	3.96	181.94	0.01
1*3	0.07	1	0.07	3.05	0.22
2*3	0.65	1	0.65	29.91	0.03
Lack of Fit	0.57	3	0.19	8.76	0.10
Pure Error	0.04	2	0.02		
Correction Total	14.95	14	0.54		

R^2=0.956; Adjusted R^2=0.884; L indicated linear effect; Q indicated quadratic effect

Table 4.10. ANOVA for Response Surface Quadratic Model for congo red onto diffrent ACs

OSACs

Source	**Sum of Squares**	**df**	**Mean Square**	**F- Value**	**Prob > F**
(1)pH (L)	91.68	1	91.6771	67.2448	0.014547
pH (Q)	5.44	1	5.4382	3.9889	0.183882
(2)Dose (L)	169.76	1	169.7630	124.5205	0.007935
Dose (Q)	45.86	1	45.8558	33.6351	0.028467
(3)Concentration(L)	7.49	1	7.4910	5.4946	0.143763
Concentration(Q)	3.05	1	3.0473	2.2352	0.273526
1L by 2L	0.14	1	0.1404	0.1030	0.778671
1L by 3L	35.36	1	35.3640	25.9394	0.036456
2L by 3L	0.05	1	0.0512	0.0376	0.864238
Lack of Fit	28.54	5	5.7083	4.1871	0.203957
Pure Error	2.73	2	1.3633		
Correction total	398.61	16			

R^2=0.9125; Adjusted R^2=0.8207; L indicated linear effect; Q indicated quadratic effect

RHACs

Source	**Sum of Squares**	**df**	**Mean Square**	**F- Value**	**Prob > F**
(1)pH (L)	47.54	1	47.54	19.35	0.05
pH (Q)	65.02	1	65.02	26.47	0.04
(2)Dose (L)	828.43	1	828.43	337.25	0.00
Dose (Q)	195.47	1	195.47	79.58	0.01
(3)Concentration(L)	63.25	1	63.25	25.75	0.04
Concentration(Q)	0.02	1	0.02	0.01	0.94
1L by 2L	0.22	1	0.22	0.09	0.79
1L by 3L	9.90	1	9.90	4.03	0.18
2L by 3L	55.86	1	55.86	22.74	0.04
Lack of Fit	89.35	5	17.87	7.27	0.13
Pure Error	4.91	2	2.46		
Correction total	1339.48	16			

R^2=0.931; Adjusted R^2=0.839; L indicated linear effect; Q indicated quadratic effect

BAGACs

Source	**Sum of Squares**	**df**	**Mean Square**	**F- Value**	**Prob > F**
(1)pH (L)	0.00	1	0.00	0.00	0.98
pH (Q)	7.51	1	7.51	2.70	0.24
(2)Dose (L)	316.14	1	316.14	113.64	0.01
Dose (Q)	1.62	1	1.62	0.58	0.53
(3)Concentration(L)	621.95	1	621.95	223.56	0.00
Concentration(Q)	201.72	1	201.72	72.51	0.01
1L by 2L	52.07	1	52.07	18.72	0.05
1L by 3L	86.53	1	86.53	31.10	0.03
2L by 3L	287.16	1	287.16	103.22	0.01
Lack of Fit	143.70	5	28.74	10.33	0.09
Pure Error	5.56	2	2.78		
Correction total	1747.63	16			

R^2=0.915; Adjusted R^2=0.805; L indicated linear effect; Q indicated quadratic effect

The sufficiency of the model was evaluated through analysis of variance (ANOVA). The ANOVA for the response surface quadratic model with two way interactions for all selected pesticides removal% onto OSACs is depicted in **Table 4.7,** onto RHACs in **Table 4.8** and BAGACs in **Table 4.9.** The model "regression coefficient (R^2) " indicating the percentage of the variability can be revealed by the model. The Lack of Fit (LOF) is the variation of the data around the fitted model. LOF is a special investigative test for adequacy of a model fit, because the effects of the additional higher-order terms are removed from the error. In this study, central points are used for calculating the pure error. If the model does not fit the data well, this will be significant. In our present study with regards to removal% onto different ACs, the LOF is not significant for all case relative to the pure error, indicating good response to the model.

The ANOVA for the response surface quadratic model with two way interactions for CR removal% onto OSACs, RHACs and BAGACs is depicted in **Table 4.10.**

4.4.6. *Standardized Pareto chart*

In order to perceive the importance of different actual factors and their interactions Standardized Pareto chart are developed by the software that are represented in **Figure. 4.13** for selected compounds by OSACs, **Figure 4.14** for RHACs and **Figure 4.15** for BAGACs according to the rank. The Vertical line which overpass through the standardized factors determine the statistical significance at 95% confidence intervals. The sign + and – reflects the positive and negative effect of the corresponding factors respectively. Positive coefficients indicate the removal is favored and negative coefficients indicate unfavorable by the factors and their interactions.

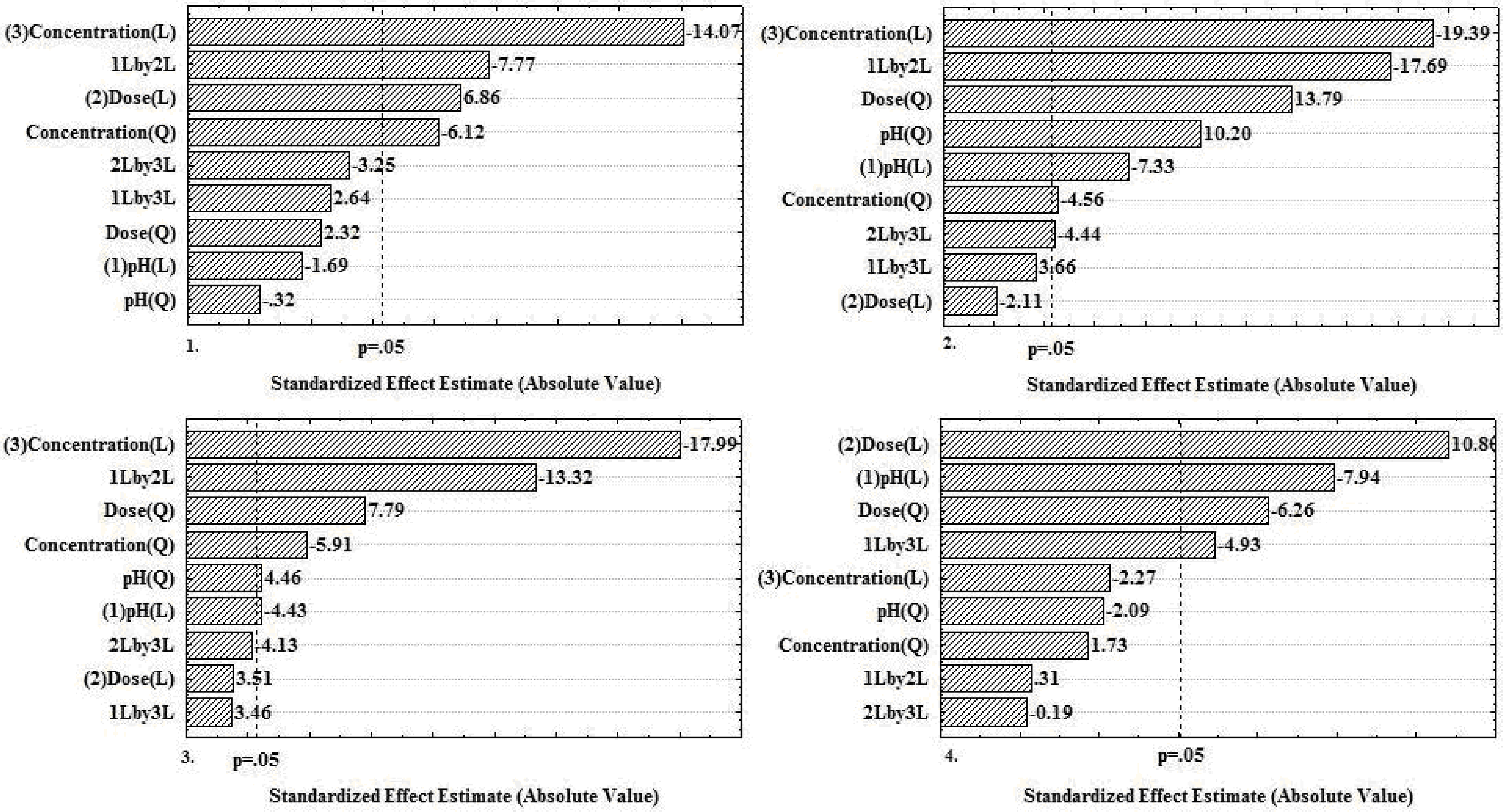


Figure 4.13. Standardized Pareto chart for main and interaction factors of 1.bromophos methyl, 2. quinalphos, 3. pretilachlor and 4. CR removal by OSACs

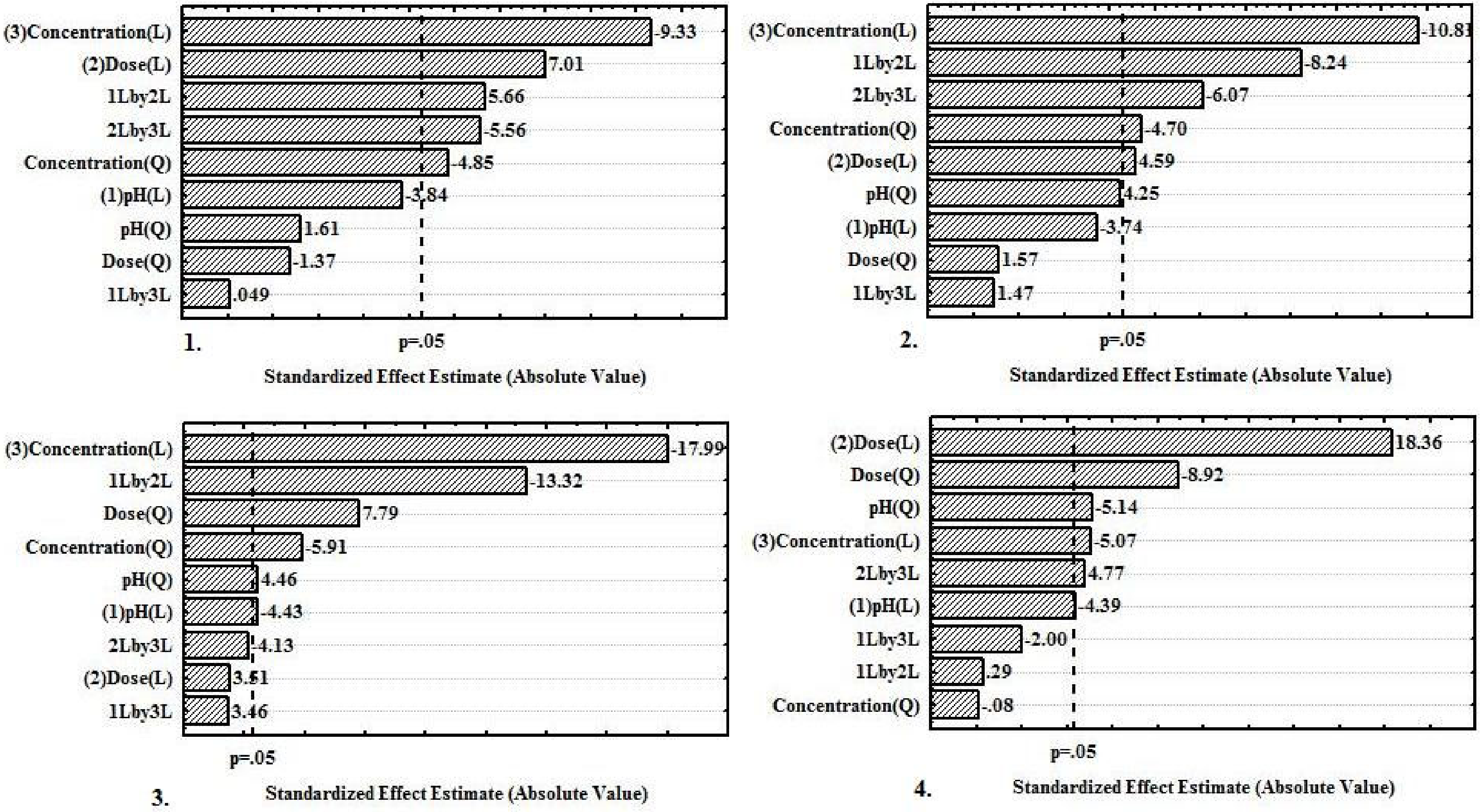


Figure 4.14. Standardized Pareto chart for main and interaction factors of 1.bromophos methyl, 2. quinalphos, 3. pretilachlor and 4. CR removal by RHACs

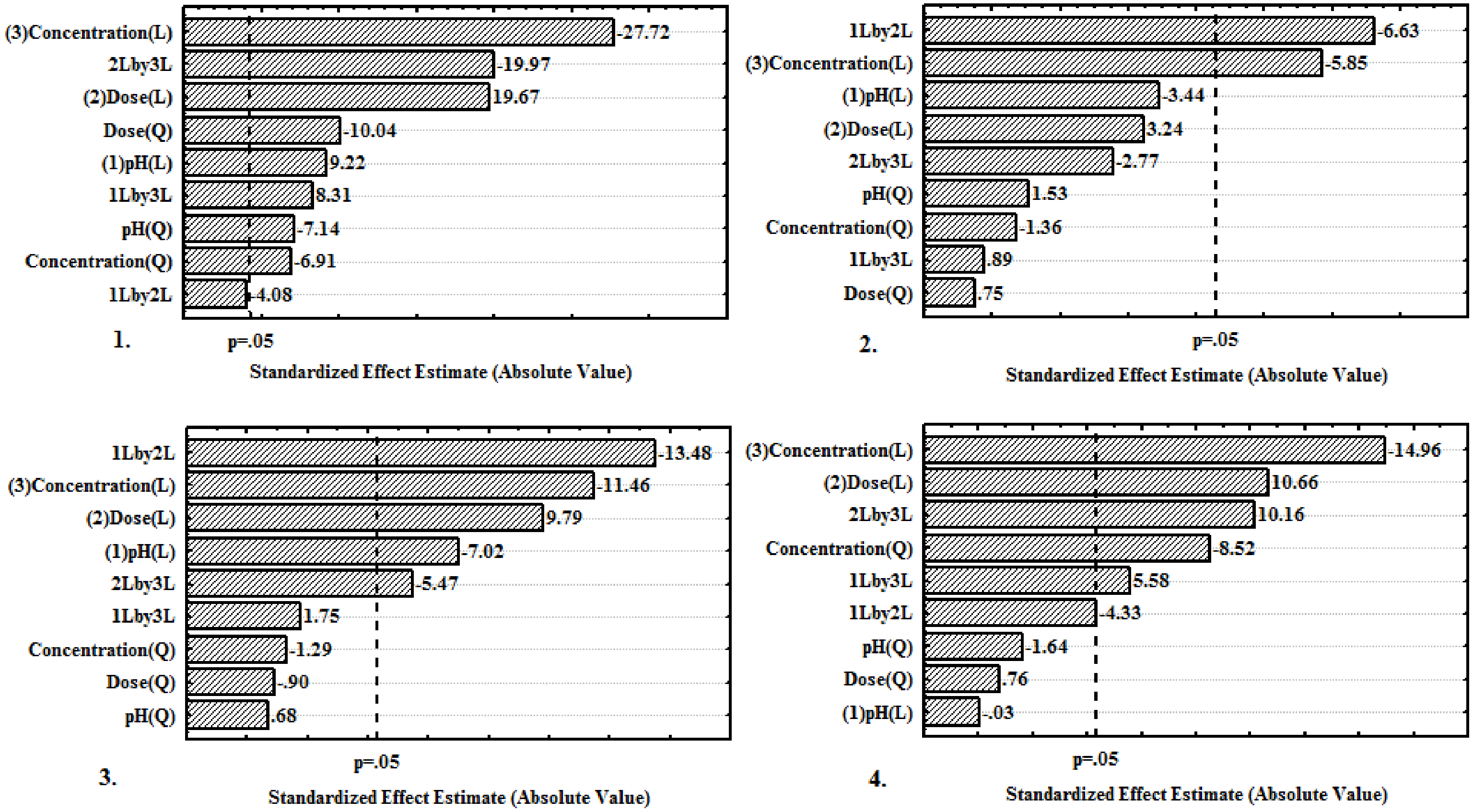


Figure 4.15. Standardized Pareto chart for main and interaction factors of 1.bromophos methyl, 2. quinalphos, 3. pretilachlor and 4. CR removal by BAGACs

4.4.7. *Models and effects of different factors on removal of selected compounds*

The final predicted mathematical model in terms of significant actual factors for bromophos methyl, quinalphos, pretilachlor and congo red removal% by different activated carbons is presented in **Table 4.11.**

4.4.7.1. Removal by OSACs

From **Table 4.11**, for bromophos methyl, it has been seen that the main effect of adsorbent dose have positive significant effect on removal percentage. If adsorbent dose increases, the removal percentage of bromophos methyl also increases. This observation attributed that the higher dosage of adsorbents increased surface area; more adsorption sites are available causing higher removal percentage. But the main effect of concentration has negative impact on removal of bromophos methyl. It is expressed if the initial concentration increases the removal percentage of bromophos methyl decrease. Suggesting limiting number of sorption sites available for sorption at higher concentration of sorbate molecules. This effect may also be interpreted that at low sorbate ion/sorbent ratios, sorbate ion sorption involves the higher energy sites. As the sorbate ion/sorbent ratio increases, the higher energy sites are saturated and sorption begins on lower energy sites, resulting in a decrease in removal efficiency (Sivaraj et al., 2001). The interaction effect of pH and dose have negative significant on removal. From **Figure 4.16a,** it has been seen that if dose and pH simultaneously increases then removal% also increases up to a certain point then decreases. This observation indicates, at certain point, surface of the OSACs is fully covered by the bromophos molecules and don't have capability to adsorb more molecules resulting lower removal percent.

From **Table 4.11,** for quinalphos, main effects of pH and adsorbent dose have positive significant impact on quinalphos removal percentage, but negative significant of concentration also observed. Quinalphos is nonionic pesticides without strong acidic or basic functionalities. The positive effect of pH on removal can be explained by the surface charge of the adsorbent and the H^+ ions present in the solution. At low pH the cations compete with the H^+ ions in the solution for the active sites and therefore lower adsorption. The surface charge of the biomass materials is a strong function of the pH. Zeta potential of OSACs particles at pH 3, 4, 5, 7 and 8 are: -8, -14.72, -18.22, -23.29, and -23.83 mV respectively. Therefore at high pH values surface of the adsorbent has a higher negative charge which results higher attraction of cations. The interactions effect of pH vs dose has negative significant impact for the removal of quinalphos onto OSACs. From **Figure**

4.16b, at high adsorbent dose with high pH gave the highest removal% until a certain point but if pH increase more than 7 then combined effect turned into lower removal of quinalphos, indicating the lack of active functional sites for excess pesticides molecules. The interaction effect of dose vs. concentration also has negative effect on removal suggesting that vacant sites of activated carbons were filled by the pesticides molecules with increasing concentration **(Figure 4.16c)**.

The main effects of pH and dose for pretilachlor have positive effect on removal as observed from **Table 4.11** but quadratic effect of these factors have negative impact on removal percentage. From **Figure 4.16d**, it has been observed that the interaction effect of pH and dose has negative impact and high ph with high dose produced lower removal percentage.

For congo red the main effect of dose positively significant on removal, indicating increases of dose increases removal percentage due to more available active surface site. In **Figure 4.16e**, it can be stated that the interaction effect of pH and concentration has negative effect on removal of CR, indicates simultaneous increases of pH and concentration will give reduced removal percentage. The highest removal% is obtained with pH and concentration in ranges of low pH and high concentrations; nevertheless, the pH effect becomes less important when the concentration level increases.

4.4.7.2. Removal by RHACs

From **Table 4.11**, it has been seen that the qudratic effcets of concentration has significant impact on removal of bromophos methtyl. The interactions effect of pH and adsorbent dose had positive significant impact on removal% of bromophos methyl as it is observed from the model and this interaction is depicted in **Figure 4.17a**. At high pH with high adsorbent dose gave the highest removal percent. It may be attributed by this fact that the adsorbent can be used in wider range of pH if higher adsorbent dose is use. **Figure 4.17b** represents the interaction effect of adsorbent dose and concentration. The removal% of bromophos methyl increases with increasing concentration and adsorbent dose but removal% was decreased after certain point of adsorbent dose, indicating that vacant sites of used tea leaves were filled by the CR molecules with increasing concentration.

For quinalphos removal by RHACs, from **Table 4.11**, it has been observed that the main effects of ph and dose had positive significant impact whereas concentration has negative significant impact on removal of quinalphos. The interaction effects of ph vs. dose and dose vs. concentration also presented in **Figures 4.17c&d**.

From **Table 4.11**, for pretilachlor, the main effcets of pH and dose also had positive significant impact on removal percentage. On the other hand main effcet of concentration had negative effect on removal of pretilachlor suggesting limiting number of sorption sites available for sorption at higher concentration of sorbate molecules. The interaction effect of ph vs dose is represented in **Figure 4.17e** indicating, at medium pH with high adsorbent dose gave the highest removal% of pesticide.

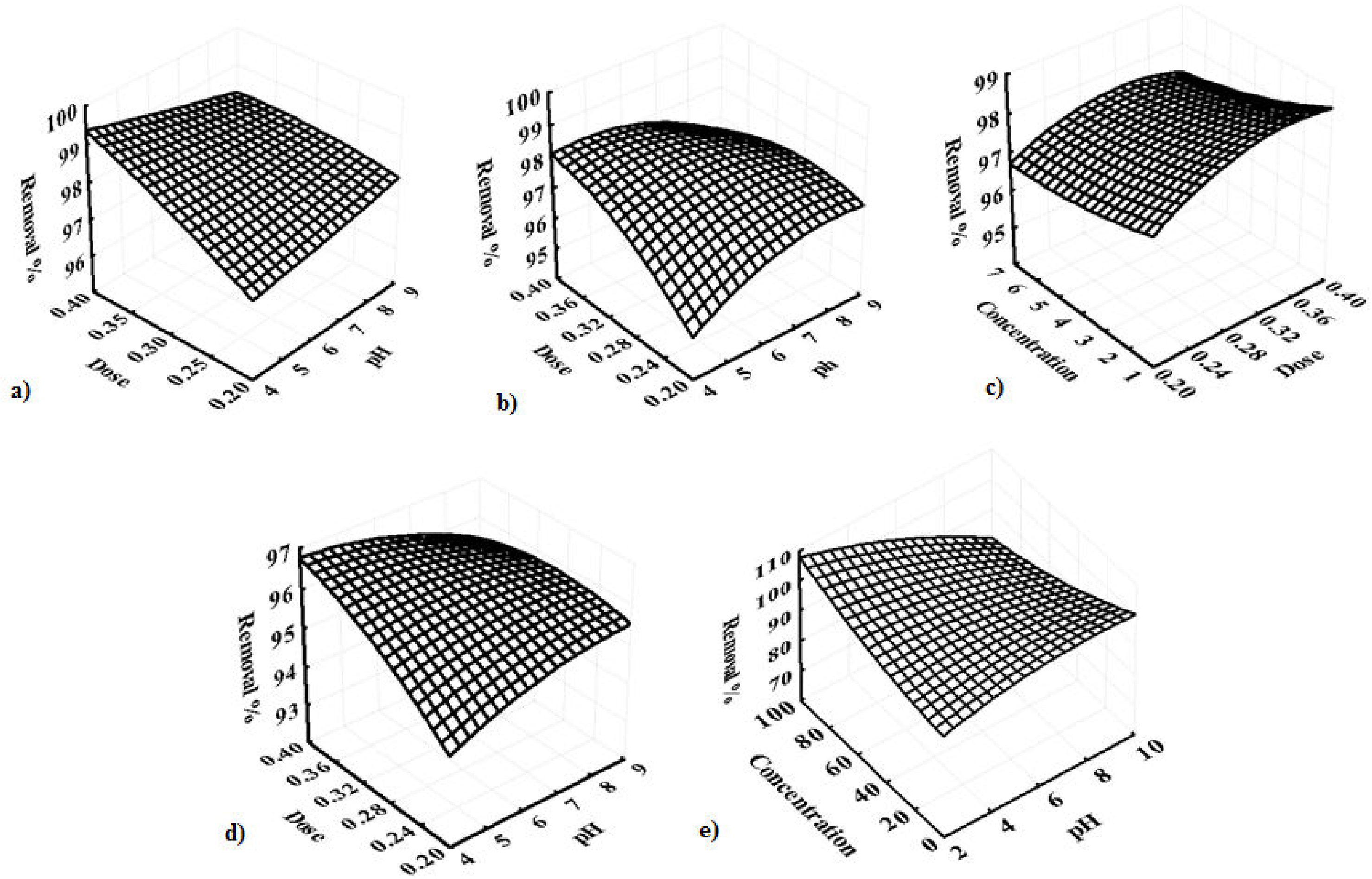


Figure 4.16. 3D response surface plots for (a) bromophs methyl, (b& c) quinalphos, (d) pretilachlor and (e) congo red onto OSACs

Table 4.11. Predicted model regression equations obtained for target compounds interms of significant actual factors

OSACs	
Compounds	Regression equations
Bromophos methyl	Removal %= 93.12 + 28.08*Dose - 0.44*Concentration + 0.035 *Concentration^{2} - 1.91*pH*Dose
Quinalphos	Removal %= 82.34 + 2.08*pH - 0.09*pH^{2} + 58.76*Dose - 50.92*Dose^{2} - 0.31*Concentration -0.02*Concentration^{2} - 3.14*pH*Dose - 0.53*Dose*Concentration
Pretilachlor	Removal %= 85.99 + 1.21*pH - 0.04*pH^{2} + 42.52*Dose - 30.42*Dose^{2} - 0.36*Concentration + 0.03*Concentration^{2} - 2.5*pH*Dose
Congo red	Removal %= 61.13 + 304.32*Dose - 795.18*Dose^{2} - 0.04*pH*Concentration

RHACs.	
Compounds	Regression equations
Bromophos methyl	Removal %= 101.18 + 0.06*Concentration^{2} + 3.12*pH*Dose - 2.05*Dose*Concentration
Quinalphos	Removal %= 81.72 + 2.23*pH + 47.23*Dose - 0.05*Concentration – 3.59*pH*Dose - 1.77*Dose*Concentration
Pretilachlor	Removal %= 86.42 + 1.22*pH – 0.04*pH^{2} + 42.73*Dose - 30.57*Dose^{2} - 0.36*Concentration + 0.03*Concentration^{2} - 2.51*pH*Dose
Congo red	Removal %= 31.72- 0.60*pH + 269.93*Dose – 416.40*Dose^{2} + 1.06*Dose*Concentration

BAGACs	
Compound	Regression equations
Bromophos methyl	Removal %= 99.45 -0.68pH + 0.06pH^{2} + 32.01*Dose^{2} + 0.02*Concentration^{2} + 0.04*pH*Concentration- 2.04*Dose*Concentration
Quinalphos	Removal %= 81.75 + 53.30*Dose - 4.85*pH*Dose
Pretilachlor	Removal %= 83.45 + 1.41*pH + 44.46*Dose - 4.98*pH*Dose - 1.35*Dose*Concentration
Congo red	Removal %= 105.55 - 0.71*Concentration – 0.01*Concentration^{2} - 12.76*pH*Dose + 0.07*pH*Concentration + 2.40*Dose*Concentration

From the zeta potential, the surface charge of RHACs is negative at 6-7 due to the different active oxygen containing functional group (-COOH, -OH etc) that obtained from FTIR analysis. Therefore, at high pH value, negatively charged surface of RHACs dissociate the anions and resulted into lower removal percent.

For congo red **(Table 4.11)** removal by RHACs, the main effcet of pH had negative significant effcet on removal of congo red. The natural zeta potential value of olive seed waste residue activated carbon was found at pH 6-7 and above this pH value, surface showed more negative values as the pH increased. As a dipolar behavior of CR, it exist anionic form at basic pH and cationic form at acidic pH. In the aqueous solution, the acid dye (CR) is first dissolved and the sulfonate groups of the acid dye (Dye-SO_3Na) are dissociated and converted to anionic dye ions. Congo red is a relatively large molecule and negatively charged for much of the pH range (>5) (Mall et al., 2005).

$$\text{Dye-}SO_3Na \rightarrow \text{Dye-}SO_3^- + Na^+$$

From the FTIR analysis it has been ensured that olive seed waste residue activated carbon surface possesses different types of active functional groups (-COOH, -OH etc.). At higher pH these surface functional groups showed anionic attitude and demonstrated antagonistic approach towards same anionic molecules of dye resulting lower adsorption. On the other hand, at lower pH, adsorption was higher. The main effect of dose had positive significant effect on removal of congo red due to more available active site for CR molecules. From **Figure 4.17f**, the interaction effect of dose vs concentration had positive significant impact on removal of CR dye. If dose increases and concentration decreases then highest removal percentage is possible. It is suggesting the increses of adsorbent dose, increses the amount of surface area of adsorbents as well as the activity of functional groups and finally produced higher removal% but increses of concentration, large molecule of CR cover the surafce gradually and resulted lower removal percentage.

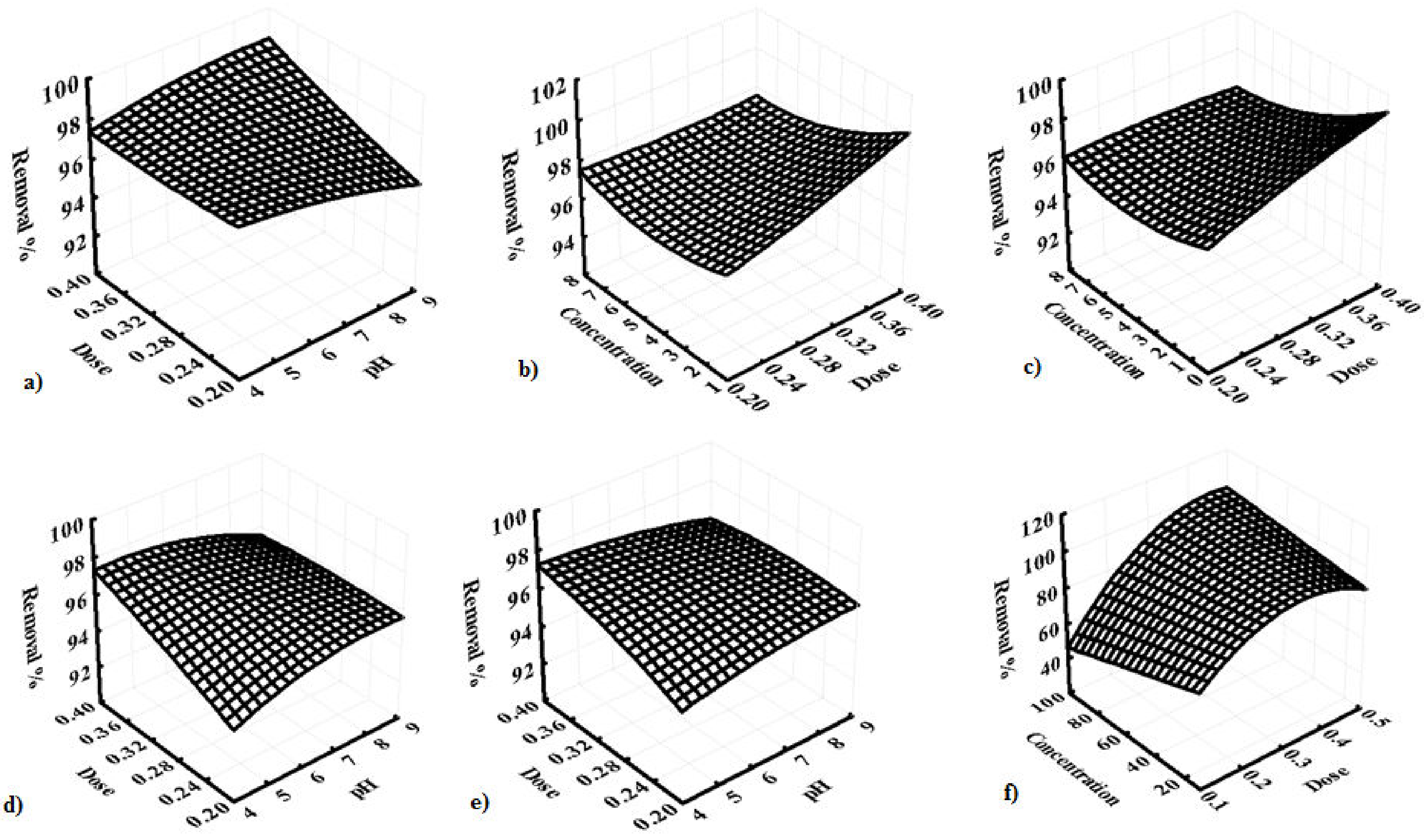


Figure 4.17. 3D response surface plots for (a & b) bromophs methyl, (c&d) quinalphos, (e) pretilachlor and (f) congo red onto RHACs

4.4.7.3. Removal by BAGACs

From **Table 4.11**, the main effect of pH has negative role on removal of bromophos methyl. The interaction effect of pH and concentration had significant positive effect on bromophos methyl removal onto BAGACs. As pH and concentration increases, anionic molecules of pesticide in solution increased and difficult for adsorbing by the adsorbent finally decrease the removal% **(Figure 4.18a)**. The lowest concentration and medium pH values gave the highest removal percentage. On the other hand, the interaction effect of dose and concentration showed negative effect on removal of bromophos methyl. As observed from **Figure 4.18b**, the removal% of bromophos increases with increasing concentration and adsorbent dose but removal% was decreased after certain point of adsorbent dose, indicating that vacant sites of used tea leaves were filled by the pesticide molecules with increasing concentration.

Adsorbent dose had high significant impact on removal of quinalphos **(Table 4.11)** removal onto BAGACs but the interaction effect of pH and dose had negative effect on removal. At high pH with high adsorbent dose gave the lowest removal% of quinalphos removal as observed from **Figure 4.18c**. This observation may be happen due to surface charge of BAGACs. From Zeta potential, at pH 6, the surface charge of BAGACs is negative. Above the pH 6, the functional groups that obtained from FTIR analysis behave anionic form, although quinalphos is a non-ionic compound, at high pH it show more polar behaviour and the surface of BAGACs attracted by the strong H+ ion rather than quinalphos molecules and resulting lower removal.

For pretilachlor removal, the main effects of pH and dose have positive significant impact on removal as observed from **Table 4.11**. The interaction effects of pH vs. dose and dose vs. concentration showed negative effect on removal of pretilachlor. From **Figure 4.18d**, it has been seen that at low pH with high adsorbent dose produced more removal percentage and on the other hand from **Figure 4.18e**, low concentration with high adsorbent dose showed the highest removal percentage of pretilachlor.

For congo red, the main effect of concentration had the negative impact on removal **(Table 4.11)**. It is expressed that if the initial concentration increases the removal percentage of CR decreases. Suggesting limiting number of sorption sites available for sorption at higher concentration of sorbate molecules. The interaction effect of pH and dose was negative, if pH increases with increasing dose then removal% was lower. But low ph with high adsorbent dose produced the highest removal percentage of CR **(Figure 4.18f)**. The interaction of pH and concentration showed positive significant impact on removal. From the **Figure 4.18g**, the highest removal% is obtained with pH and concentration in ranges of low pH and low concentrations; nevertheless, the pH effect becomes less important when the concentration level increases. **Figure 4.18h**, represents the interaction effect of adsorbent dose and concentration. The removal% of CR increases with increasing concentration and adsorbent dose but removal% was decreased after certain point of adsorbent dose, indicating that vacant sites of used tea leaves were filled by the CR molecules with increasing concentration.

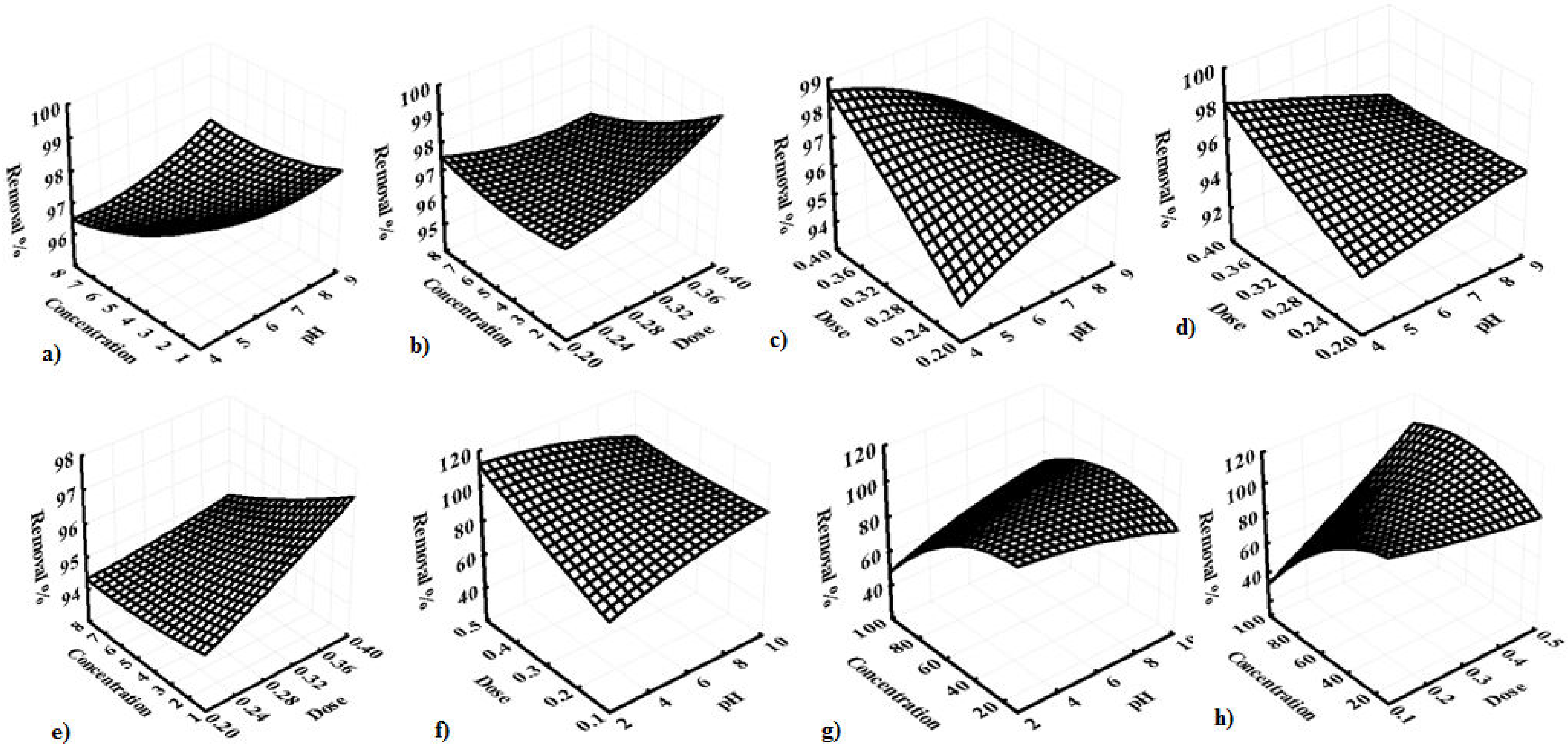


Figure 4.18. 3D response surface plots for (a & b) bromophs methyl, (c) quinalphos, (d&e) pretilachlor and (f,g&h). congo red onto BAGACs

4.4.8. *Optimization by using desirability function*

The optimization process was done by selecting software profile and desirability option. The detailed mathmatical appraoches of desirability function is described in section 2.7.1.5 of chapter two. A prediction profile for a dependent variable consists of a series of graphs, one for each independent variable, of the predicted values for the dependent variable at different levels of one independent variable, holding the levels of the other independent variables constant at specified values, called current values. If appropriate current values for the independent variables have been selected, inspecting the prediction profile can show which levels of the predictor variables produce the most desirable predicted response on the dependent variable.

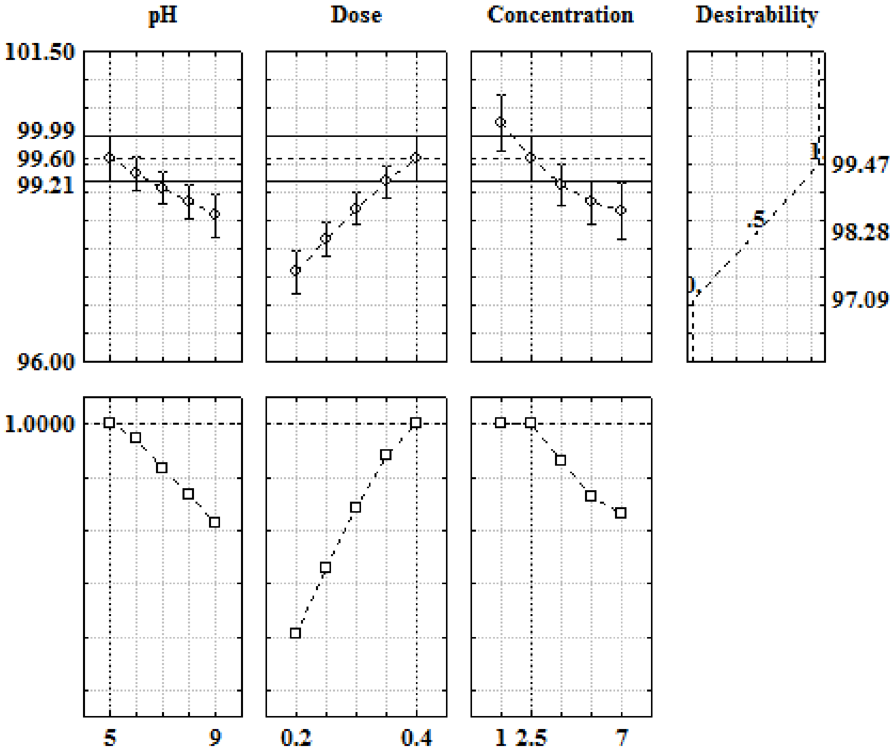


Figure 4.19. Profiles for predicated values and desirability function for bromophos methyl removal% by OSACs. Dashed line indicated current values after optimization

For example, bromophos methyl removal by OSACs, the Box-Behnken design matrix results from **Table 4.2**, represented maximum removal% (99.47%) was assigned as desirability 1.0, minimum (98.28%) as desirability 0.0 and middle (97.09%) as desirability 0.5 **(Figure 4.19)**. Afterwards, the predicted responses at each level of each factor, holding all other factors constant at their current setting are calculated and the individual desirability scores for the predicted values for each dependent variable are then combined by computing their geometric mean. By this way, software executes the calculation and finally gives the predicted responses at the current level of each factor in the model. On the basis of above calculations and choosing desirability score of 1, the best optimized conditions were found to be pH 5, dose 0.40 g and concentration 2.5 mg L^{-1} that also optimized 99.60% removal of bromophos methyl by utilizing OSACs.

The individual desirability scores of each parameter are illustrated in **Figure 4.19** (bottom). Since our target is to obtain desirability 1, therefore, the factor levels (5, 0.40 and 2.5) were chosen only when they meet our target as well as desirability 1 and finally produce maximum response (99.60 %) in the same level that is presented at the top (left) of **Figure 4.19**. For example, if concentration 1 would be selected as optimized factor value (although this point showed individual desirability 1 with the highest removal%) whiles other factors are constant at the same levels (dose 0.25 and pH 6), this pH value optimized more than 99.60 removal % and this is not in the same removal% levels of other selected overall desirability values for specific factors.

In the similar way, optimization by desirability function was adopted in order to determine the optimum factors as well as response (removal %) for all compounds (including CR from CCD) onto different ACs **(Figure 4.20-4.27)**

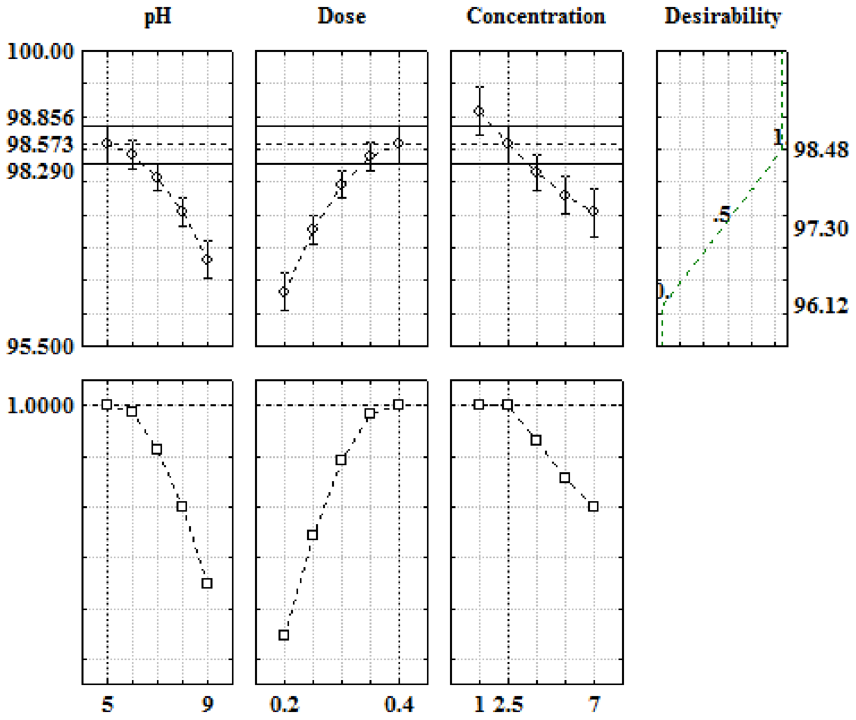


Figure 4.20. Profiles for predicated values and desirability function for quinalphos removal% by OSACs. Dashed line indicated current values after optimization

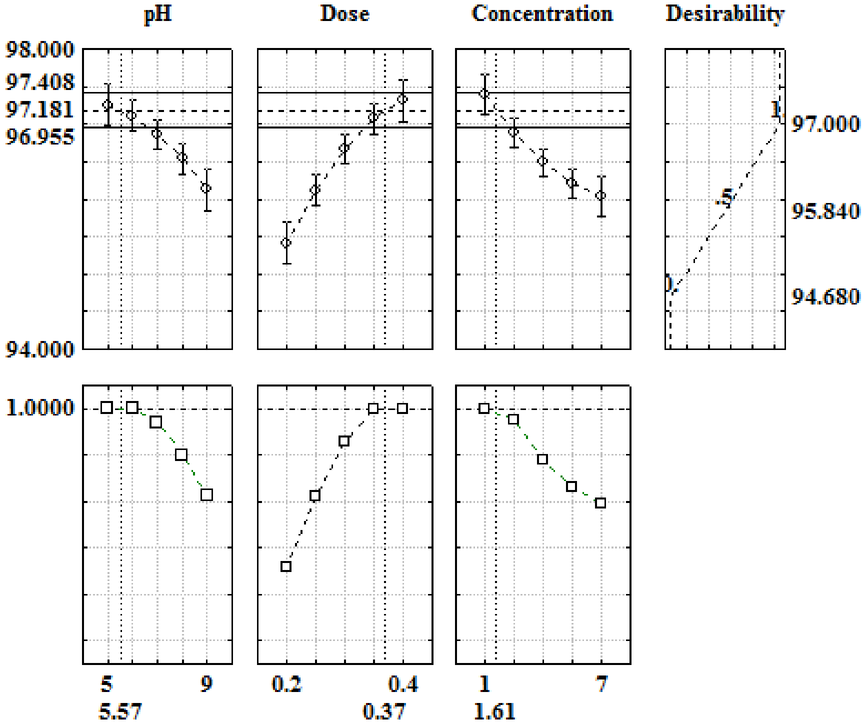


Figure 4.21. Profiles for predicated values and desirability function for pretilachlor removal% by OSACs. Dashed line indicated current values after optimization

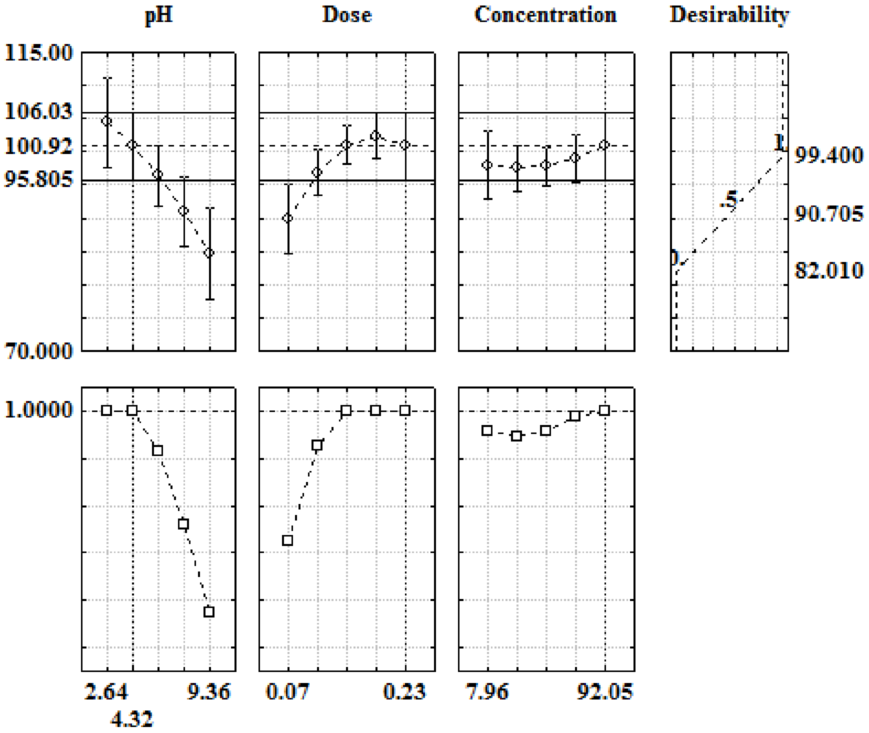


Figure 4.22. Profiles for predicated values and desirability function for congo red removal% by OSACs. Dashed line indicated current values after optimization

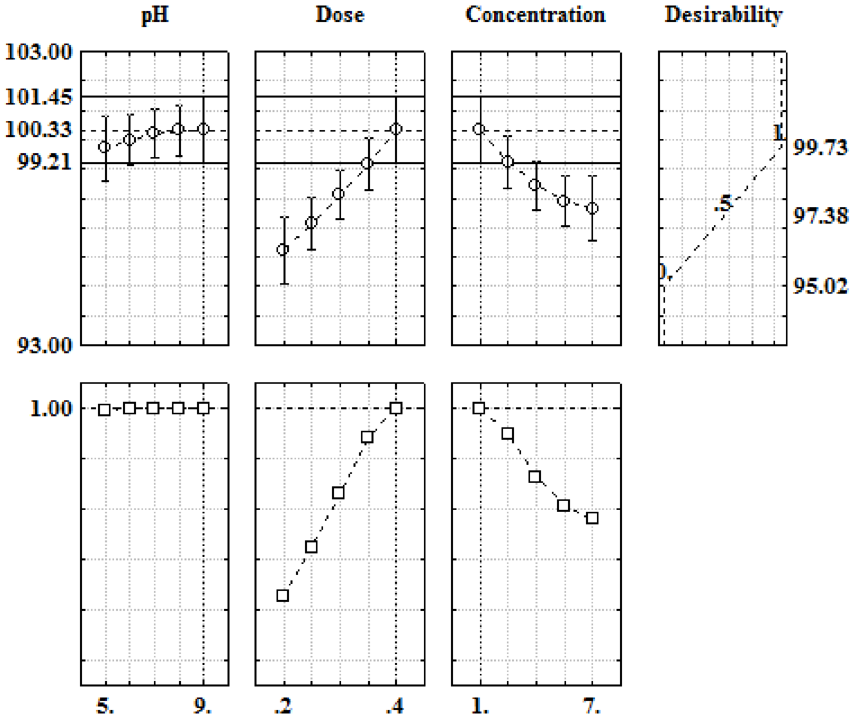


Figure 4.23. Profiles for predicated values and desirability function for bromophos methyl removal% by RHACs. Dashed line indicated current values after optimization

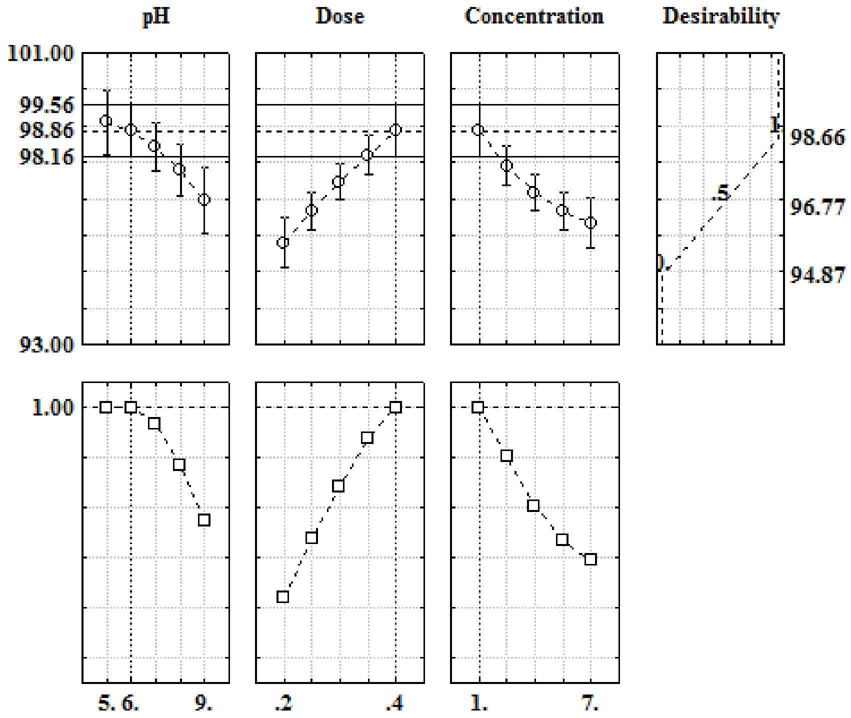


Figure 4.24. Profiles for predicated values and desirability function for quinalphos removal% by RHACs. Dashed line indicated current values after optimization

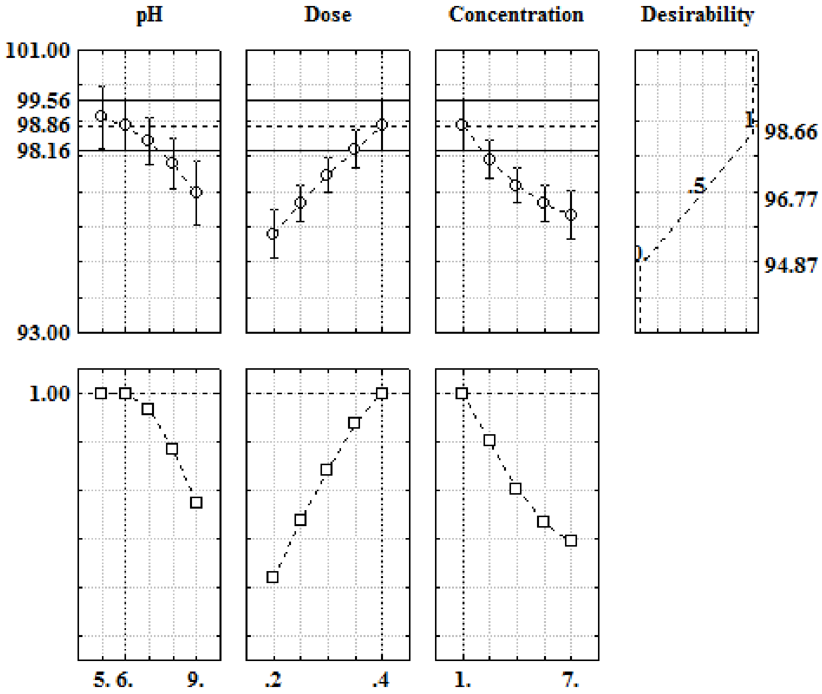


Figure 4.25. Profiles for predicated values and desirability function for pretilachlor removal% by RHACs. Dashed line indicated current values after optimization

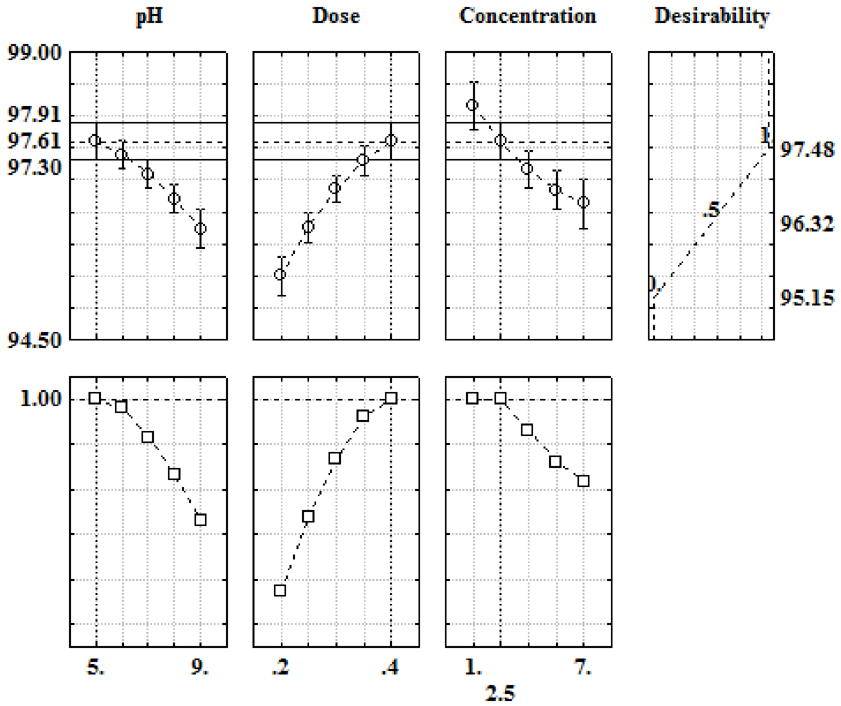


Figure 4.26. Profiles for predicated values and desirability function for congo red removal% by RHACs. Dashed line indicated current values after optimization

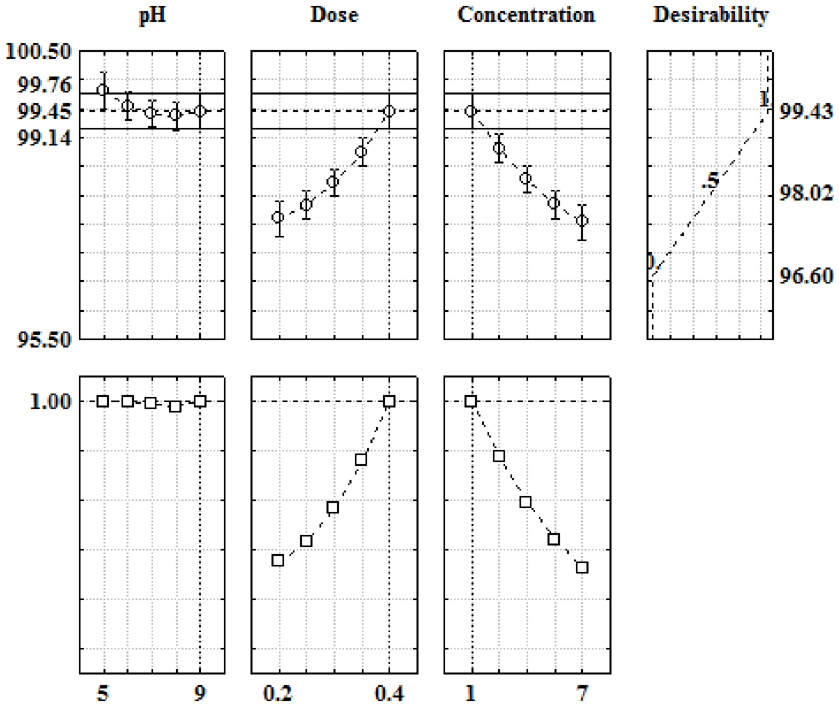


Figure 4.27. Profiles for predicated values and desirability function for bromophos methyl removal% by BAGACs. Dashed line indicated current values after optimization

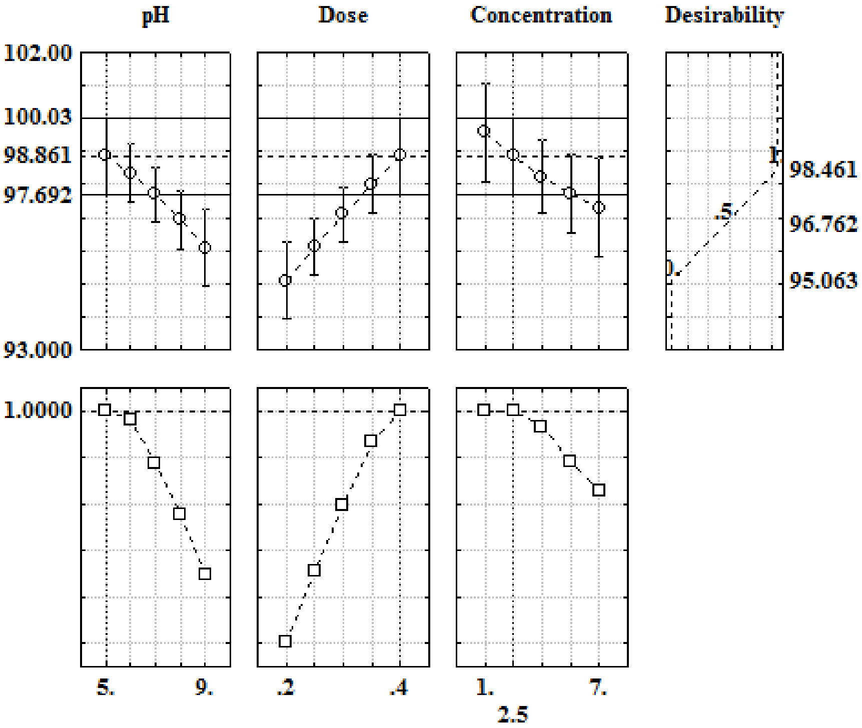


Figure 4.28. Profiles for predicated values and desirability function for quinalphos removal% by BAGACs. Dashed line indicated current values after optimization

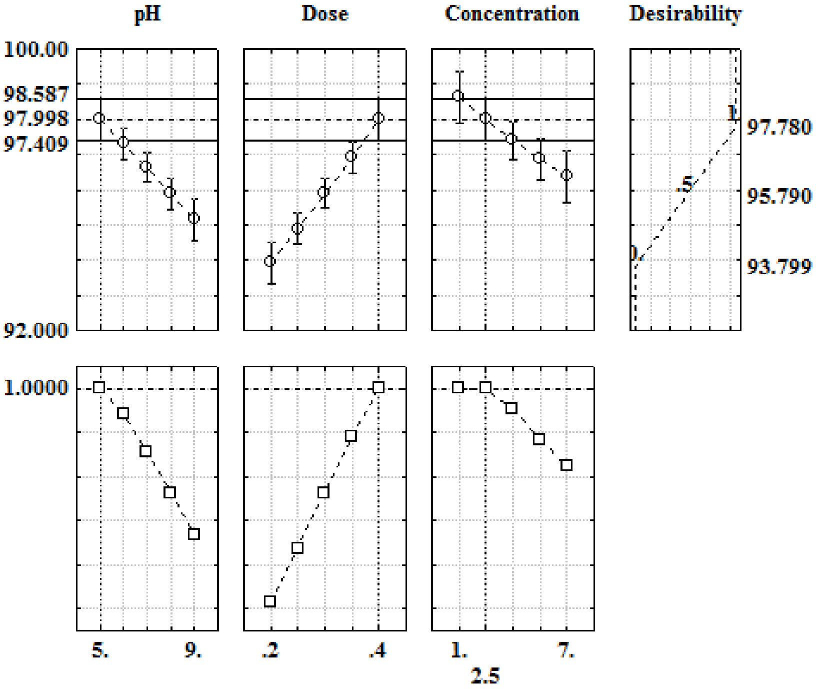


Figure 4.29. Profiles for predicated values and desirability function for pretilachlor removal% by BAGACs. Dashed line indicated current values after optimization

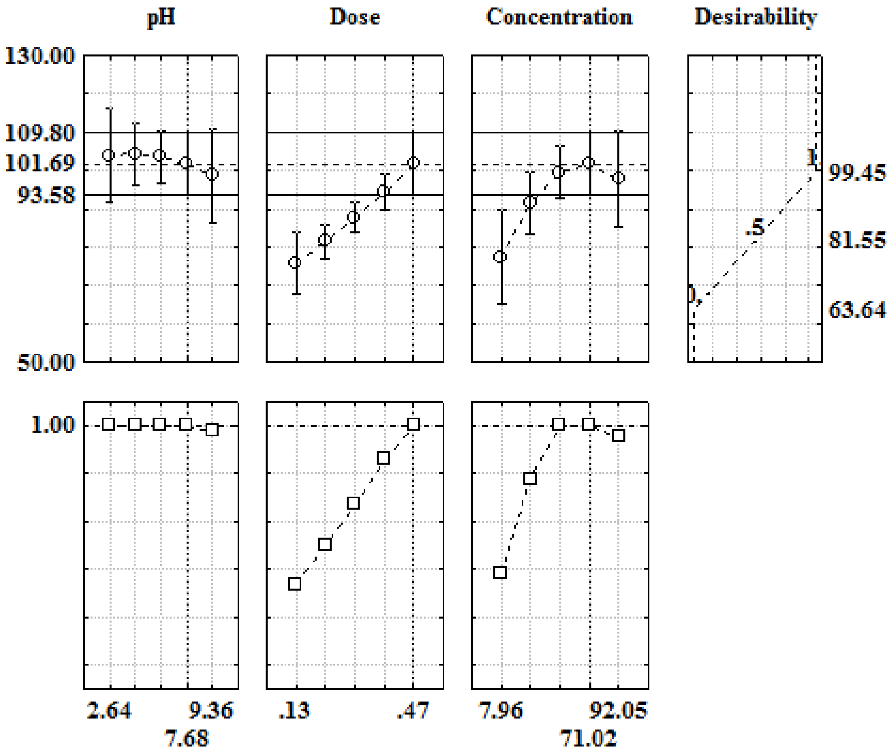


Figure 4.30. Profiles for predicated values and desirability function for congo red removal% by BAGACs. Dashed line indicated current values after optimization

All the above aptimized factors value with their coresponding removal percentage for all compounds onto different ACs are summarized in **Table 4.12**.

4.4.9. *Model validation*

Finally, validation as well as duplicate assenting experiment was performed using the optimized parameters obtained from multivariate RSM design for all compounds by selected adsorbents. The results are closely correlated with the data obtained from optimization analysis using Box-Behnken and CCD, indicating that RSM could be effiectively used to optimize the removal% for the studied adsorbents.

Tale 4.12. Optmium values obtained from RSM based on desirability function and selected factors with their corresponding removal% for all pesticides and dye onto ACs

		Optimum value		
		Bromophos methyl		
Materials	pH	Adsorbent dose(g)	Concentration (mg/L)	Removal %
Olive seed waste AC	5	0.40	2.5	99.60
Rice husk AC	9	0.40	1.0	100.33
Bagasse AC	9	0.40	1.0	99.45
		Quinalphos		
Olive seed waste AC	5	0.40	2.5	98.57
Rice husk AC	6	0.40	1.0	98.86
Bagasse AC	5	0.40	2.5	98.86
		Pretilachlor		
Olive seed waste AC	5.6	0.38	1.61	97.18
Rice husk AC	5	0.40	2.5	97.61
Bagasse AC	5	0.40	2.5	97.99
		Congo red		
Olive seed waste AC	4.32	0.23	92.05	100.92
Rice husk AC	4.32	0.47	92.05	100.04
Bagasse AC	7.68	0.47	71.02	101.69

4.4.10. *Adsorption isotherm*

In order to assess the potential adsorption capacity of the all selected activated carbon toward the pesticides and dye studied, adsorption isotherms at room temperature were derived on the basis of batch analysis with constant dose and pH obtained from the statistical optimization by desirability functions that has been presented in **Table 4.12**. Adsorption isotherm studies were carried out in 15 ml polypropylene centrifuge tubes with 10 ml of the different pesticides initial concentrations (0.5, 1.0, 2.5, 5.0 and 7 mg L^{-1}). For CR, 50 ml polypropylene centrifuge tubes with 25 ml of the different CR initial concentrations (10, 25, 50, 75 and 100 mg L^{-1}) were examined. The extraction and analysis procedures were followed according to the previously discussed section 2.3 and 2.4. The amount adsorbed (q_e) by the selected adsorbents was calculated by the following equation (4.5)

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{4.5}$$

where, C_0 and C_e are the initial and equilibrium concentrations (mg L^{-1}), V is the volume of solution (L) and m is the mass of the activated carbons (g)

The Freundlich isotherm is widely employed for sorption surfaces with non-uniform energy distribution can be expressed **(Equation 4.6)** as

$$q_e = K_F C_e^{1/n} \tag{4.6}$$

The Langmuir isotherm is mainly applied to monolayer adsorption, can be described **(Equation 4.7)** as

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{4.7}$$

All the adsorption isotherms were constructed for activated carbon using the linearized Freundlich **(Equation 4.8)** and Langmuir **(Equation 4.9)** isotherm equation by plotting log (q_e) versus log(C_e) and $1/q_e$ versus $1/C_e$ respectively.

$$\log q_e = \log(K_F) + \frac{1}{n}\log(C_e) \tag{4.8}$$

$$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \tag{4.9}$$

where,

q_e is the adsorbed amount (mg g^{-1}),

C_e is equilibrium concentration (mg L^{-1}),

K_F is the Freundlich coefficient that represents the degree or strength of adsorption.

$1/n$ is an exponential coefficient that reflects the curvature in the isotherm.

q_m (mg g^{-1}) is the maximum adsorption capacity of the adsorbent;

K_a is the Langmuir's constant.

X_m is the adsorption capacity (mg g^{-1}),

Table 4.13. Adsorption isotherm values of bromophos methyl, quinalphos, pretilachlor and congo red by Freundlich and Langmuir models

		Freundlich				**Langmuir**		
Com	Parameters	OSACs	RHACs	BAGACs	Parameters	OSACs	RHACs	BAGACs
Bromophos	K_F (mg g^{-1}(mg l^{-1})$^{-1/n}$)	1.80	1.92	1.72	q_m (mg g^{-1})	11.11	5.26	1.23
	1/n	1.20	1.11	1.16	K_a (l mg^{-1})	0.145	0.505	1.466
	R^2	0.935	0.980	0.946	R^2	0.975	0.992	0.976
	F_{error}	2.308	2.282	2.245	F_{error}	0.115	0.071	0.101
Quinalphos	K_F (mg g^{-1}(mg l^{-1})$^{-1/n}$)	1.16	1.20	1.5	q_m (mg g^{-1})	8.13	1.67	1.59
	1/n	1.19	1.15	1.18	K_a (l mg^{-1})	0.162	0.517	0.788
	R^2	0.945	0.948	0.935	R^2	0.973	0.964	0.966
	F_{error}	2.171	1.962	2.154	F_{error}	0.115	0.107	0.120
Pretilachlor	K_F (mg g^{-1}(mg l^{-1})$^{-1/n}$)	1.16	1.10	1.3	q_m (mg g^{-1})	4.00	1.52	1.16
	1/n	1.09	0.91	1.04	K_a (l mg^{-1})	0.477	1.04	1.323
	R^2	0.967	0.930	0.988	R^2	0.988	0.978	0.988
	F_{error}	0.211	1.807	0.125	F_{error}	0.078	0.013	0.054
Congo red	K_F (mg g^{-1}(mg l^{-1})$^{-1/n}$)	1.93	2.50	1.22	q_m (mg g^{-1})	33.90	6.08	3.27
	1/n	0.490	0.52	0.3930	K_a (l mg^{-1})	0.147	10.60	2.112
	R^2	0.985	0.916	0.978	R^2	0.947	0.991	0.985
	F_{error}	0.3290	0.209	0.193	F_{error}	0.0155	0.007	0.041

Langmuir and Freundlich isotherms parameters for the adsorption of all compounds onto different activated carbons are given in **Table 4.13**. The experimental isotherms data to Freundlich and Langmuir equations seems to be quite good regarding linearity. But only R^2 values cannot revealed the better fitting of the model, for these, all the models were evaluated by error function in order to find out the best fit isotherm model, the error function can be expressed **(Equation 4.10)** as:

$$F_{error} = \sqrt{\frac{\sum_i^p ((q_i cal - q_i \exp)/q_i \exp)^2}{p}} \tag{4.10}$$

where, $q_i\, cal$ is each value of q_e predicted by the fitted model and $q_i \exp$ is each value of q_e measured experimentally, and p is the number of experiments conducted.

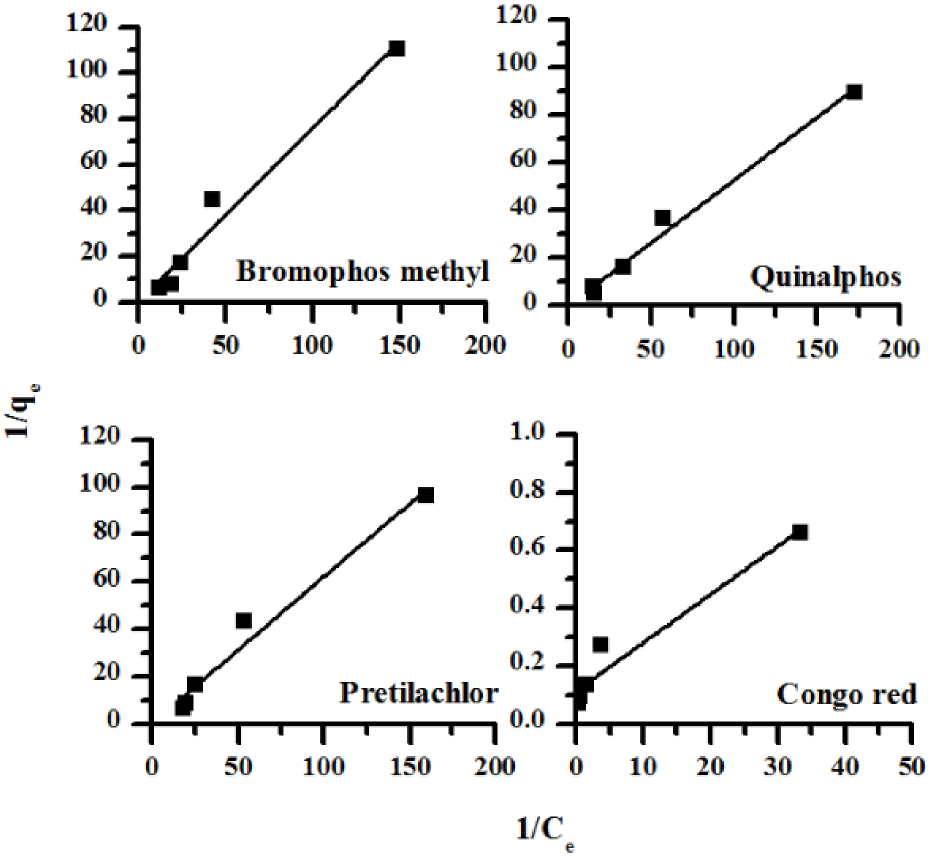


Figure 4.31. Langmuir isotherm plots of different compounds on OSACs

By comparing the results of the values of error function presented in **Table 4.13**, it can be concluded that the Langmuir model best fits the adsorption isotherm data for all activated carbons **(Figures 4.31, 4.32 and 4.33)**. Similar results were also reported for the removal of pesticides and CR dye onto activated carbon (Hameed et al., 2009;Lorenc-Grabowska and Gryglewicz, 2007; Domingues et al., 2007).

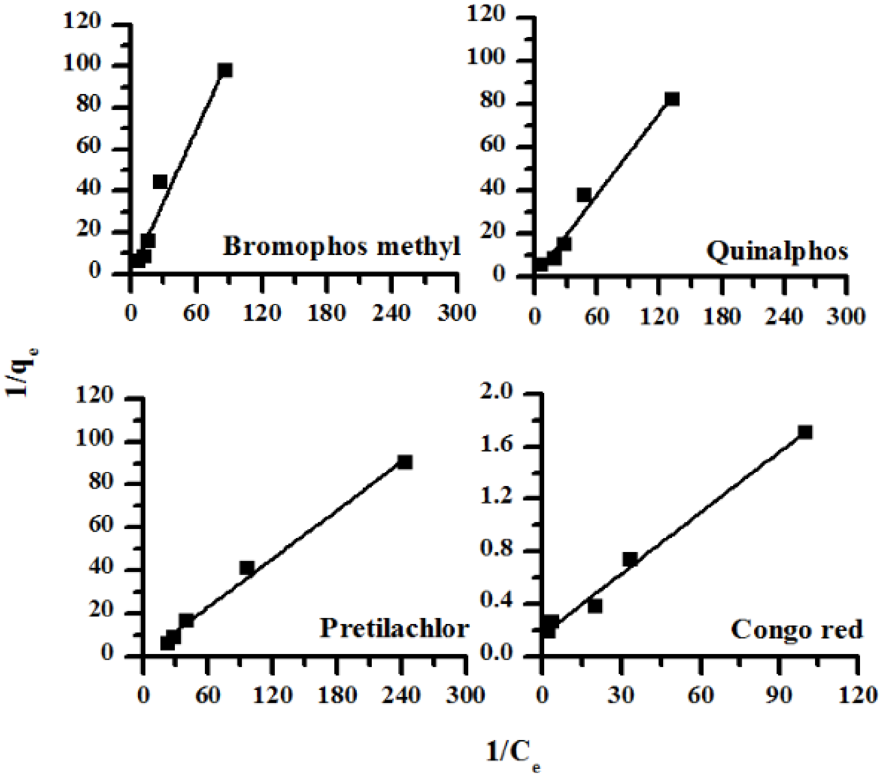


Figure 4.32. Langmuir isotherm plots of different compounds on RHACs

The monolayer adsorption capacity of olive seed waste residue activated carbon (OSACs), q_m, were found to be the highest for all compounds in comparison to other activated carbon studied. This observation attributed that higher surface area of activated carbon play a vital role for the removal of organic pollutants from the aqueous solution. Therefore, it can be infer from this study that olive seed waste residue activated carbons are potential adsorbents for removing hazardous from waste water.

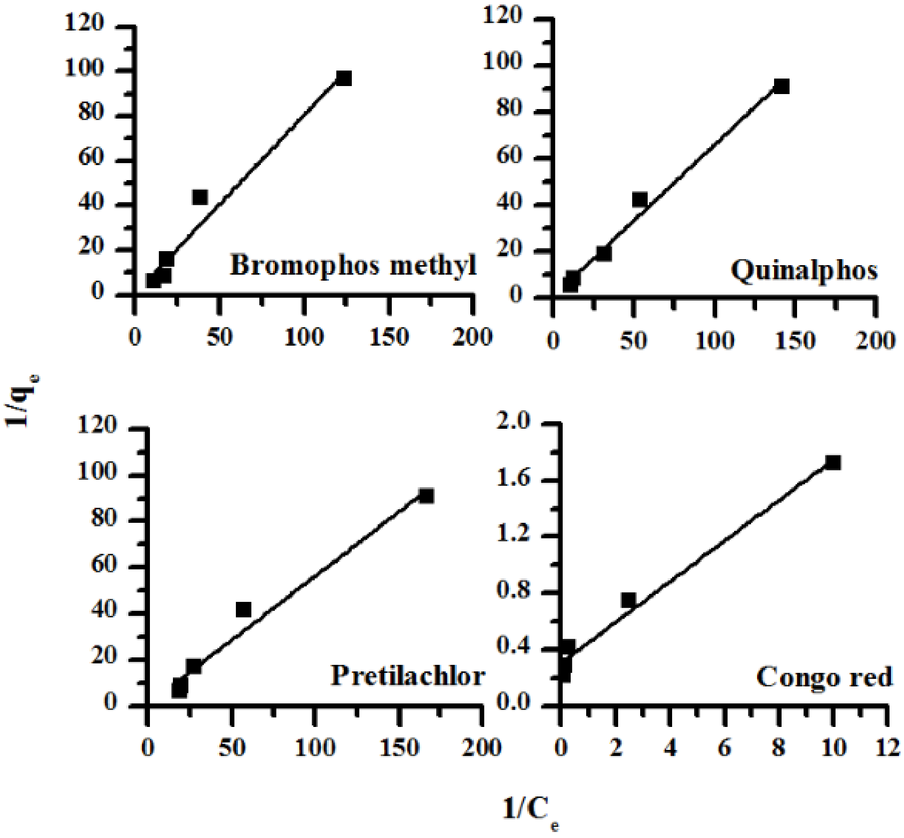


Figure 4.33. Langmuir isotherm plots of different compounds on BAGACs

4.5. Conclusion

In the present study the analytical utility of multivariate chemometric techniques in the investigation of different selected compounds removal has been demonstrated. RSM was applied successfully in order to establish a relationship among the different removal processing factors (pH, adsorbent dose and concentration) with response (removal%), moreover, desirability function was used to identify optimum removal% by calculating specific factors optimization simultaneously. The experimental results showed that olive seed activated carbons, rice husk activated carbon and bagasse activated carbons can be used as effective adsorbent for the removal of bromophos methyl, quinalphos, pretilachlor and congo red dye from water, the removal being dependent on pH, adsorbent dose and concentration of the compounds. The pseudo-second order kinetics showed better results for adsorption process in the way of equilibrium for all compounds on all activated carbons indicate chemosorption. The Langmuir isotherm model was the best-fitted with regard to isotherm for all cases. Therefore, from this study, it may be also concluded that the use of statistical methods by response surface methodology with desirability function can be optimized well by avoiding unnecessary experiments providing a further perspicacity for potential use of other processes.

CHAPTER V

REMOVAL OF BROMOPHOS METHYL, QUINALPHOS, PRETILACHLOR AND CONGO RED DYE ONTO DIFFERENT LOW COST MATERIALS BASED ON RESPONSE SURFACE METHODOLOGY

Abstract

This work deals with the multiple response optimization for removal of bromophos methyl, quinalphos, pretilachlor and congo red dye from the aqueous solution onto low cost material and tried to overcome the drawbacks of univariate optimization. Neem leaves powder (NLP), used tea leaves (UTL) and sawdust (SD) was used as low cost adsorbents and batch equilibration method was followed for this study. A Box-Behnken design was used to develop response model and desirability function was then used for simultaneous optimization of all affecting parameters in order to achieve the highest removal% of all pesticides. And central composite design (CCD) was used for congo red (CR) removal. Considering the optimum conditions obtained by using desirability function, the adsorption isotherms were developed and indicated the suitability of adsorption data to Langmuir equation. Kinetics studies were also performed and the kinetic data fits to pseudo second order model well than pseudo first order model. Therefore, this study indicating that NLP and UTL may be applied as low cost materials for pesticides and dye removal from aqueous matrices.

5.1. Introduction

The usage of organic pesticides is increasing day by day with increasing world population, especially organophosphorus pesticides (OPPs) due to their relatively low persistence in the environment and by the transfer from highly persistent organochlorine pesticides. The toxicity effects of OPPs were well documented by several workers (Aardema et al., 2008; IEH, 2002; Carey, 1999). The OPPs are in general categorized into four subgroups according to molecular structures: phosphates, phosphorothioates, phosphorodithioates, and phosphorothiolates (Pehkonen and Zhang, 2002). Among them, phosphorothioates group, in which phosphorus atom (P) is bound to three oxygens and one sulfur (the double bond), are used extensively all over the world. Quinalphos and bromophos methyl is phosphorothioates group OPPs that has an acetylcholinesterase (enzyme) inhibition property. Many studies have also been documented about the toxicity of quinalphos and its metabolites (2-hydroxyquinoxaline) on plants and soil microorganisms (Vig et al, 2006), humans, laboratory animals and several wildlife species including aquatic and terrestrial (Riediger et al., 2007; Vasilic et al., 1992; Durairaj and Selvarajan, 1992; Rupa et al., 1991; Rupa et al., 1990).

Acetanilide herbicides are widely used for preemergence control of broad-leaved weeds in corn, soybean and several other crops (Wang et al., 1999). Pretilachlor is one of the most used acetanilide herbicides applied in the rice paddy field (Kibe et al., 2000; Balasubramanian et al., 1999). Pretilachlor is suspected to Kidney Toxicant (RTECS, National Institute for Occupational Safety and Health's Registry of Toxic Effects of Chemical Substances). A recent study revealed the excessive exposure of pretilachlor to pregnant women and child (Ostrea et al., 2009). The ignorant or deliberate discharge of pesticides into adjacent water courses, via, for example, leaky stores, careless disposal of containers, and direct spraying, is generally causing to the surface and ground water contamination by theses pesticides. Therefore, these compounds are potential hazards to human health as well as ecosystems by surface and ground water contamination.

Synthetic dyes are very important for textile and yarn dyeing industries, carpet industries and other dye based industries due to its availability and costs than natural dyes. Among the all synthetic dyes, azo dyes are mostly common used dyes for its easy synthesize. Like pesticides, some azo dyes possess toxic uniqueness and liable for human carcinogen and mutagen. Toxic water released from several yarn dyeing and processing mills are polluting the local environment, causing myriad suffering to the adjacent people and posing serious health hazard by contaminating surface water bodies. Congo red is one of the most frequently used secondary diazo dye of benzidine based origin and it metabolizes to benzidine, which is a known to human carcinogen and mutagen. Congo red effluents are highly colored; contain high amounts of dissolved solids (Maiti et al., 2008). Moreover, CR is durable to biodegradation that is potential threat to the environment (Mall et al., 2005).

Adsorption is one of the most recognized methods used in the removal of such hazardous substances from polluted water. For this, activated carbon is the most widely used material for removal of organic pollutants ((Purkait et al., 2007; Pikaar et al., 2006; Ayranci and Hoda, 2005). As we already know from the previous chapter, activated carbons (ACs) are very effective for removal of pollutants from aqueous solution. But the use of activated carbons sometimes restricted in view of higher cost. Also, the activated carbons after their use (treatment of wastewater) become exhausted and regenerations of ACs involve sophisticated mechanisms that need higher costs. It is also true that regeneration process results in a loss of carbon and the regenerated product may have a slightly lower adsorption capacity in comparison with the virgin activated carbon (Gupta and Suhas, 2009).

So it is an urgent need to search low-cost materials for the removal of pesticides and hazardous dye from waste water. In recent times, many studies have reported about the application of various low cost materials of diverse origin for removal of pesticides from aqueous solution. These include watermelon peels (Memon, et al., 2008), rice husk (Akhtar et al., 2007) etc. In this study, Neem leaves powder, used tea leaves and saw dusts were used as a low cost materials for the removal of all selected pesticides and dye. According to our knowledge, no work has been done for the removal of pesticides from aqueous solutions onto used tea leaves with statistical design of experiments.

It is factual that only the use of low cost materials cannot ensure the desired output of removal efficiency if the processes or input parameters are not well optimized, organized and efficient. The conventional one factor at a time approach to optimization is time-consuming, non-feasible and inept of getting the true optimum condition due to lack of interactions among the factors. For this reason, Response Surface Methodology (RSM) is now days a widely used statistical tool for process optimization through a relatively smaller number of systematic experiments that can reduce time, cost and resources. In the present study, RSM with Box-Behnken design and Central composite design (CCD) was successfully employed to verify the various interactions of responsible factors for removal of selected compounds. Besides, the desirability function for optimization of adsorption process was employed in order to develop an efficient method for achieving maximum removal% of selected compounds from the aqueous solutions by combination of all optimized input factors and, an optimized response model was proposed. Finally, removal capacities of all adsorbents were determined by considering all optimized factors.

5.2. Specific objectives of the study

- to determine the kinetic model which suited best to the removal data.
- to removal of selected 3 pesticides and one dye from aqueous solution by selected low cost materials based on response surface methodology.
- to identify the interaction between the parameters and optimization using desirability function.
- to developed isotherm models by using optimized factors obtained from desirability function optimization and
- to determine the adsorption capacity of selected materials in order to remove selected hazardous compounds.

5.3. Materials and methods

5.3.1. *Adsorbents*

5.3.1.1. Preparation of used tea leaves

The manufactured used tea leaves (tea bags) were collected from local cafeteria. Leaves were washed thoroughly by normal water and afterwards with double distilled water for removal of pigments and impurities. After drying 3 days in room temperature, leaves were placed in the oven at 80 ^{0}C for removing of extra moisture and before stored for further use, tea leaves were sieved in order to find particle size ranges of 0.710-1.00mm according to US standard testing sieves. No other physical and chemical treatments were performed before experiments. Precautions were taken to avoid contamination during drying and storage.

5.3.1.2. Neem leaf powder as an adsorbent

Azadirachta indica A. Juss. a member of the Meliaceae family is widely known as neem, a tree that found throughout the dry tropics and subtropics (Tewari, 1992; Troup, 1921). During last three decades neem has been established as a versatile multi-purpose tree species that could be used for agriculture, forestry, medicine and household purposes (Koul et al., 1990). The main chemical ingredients of various neem tree parts belonging to the triterpene or limnoid group and the main components in neem are azadirachtin, salannin, meliantriol, nimbin and nimbidin. Besides, there has large number of functional groups on neem leaves powder (Bhattacharyya and Sharma, 2004). Skellon et al., 1962 found a number of fatty acids like steric acid, oleic acid, linoleic acid, palmitic acid etc. in neem leave.

The green leaves were collected from Jessore, Bangladesh. Leaves were washed through normal water and dried well in the open sunlight until crispy form. Then dried leaves were crushed by mechanical grinder to make powder and sieved through a 0.05-.074-mm mesh. Afterwards these powders were washed thoroughly with double distilled water until colorless for removal of pigments and impurities. After drying 3 days in room temperature, leaves were placed in the electric oven at 80 ^{0}C temperature for removing extra moisture and stored for further uses.

5.3.1.3. *Collection and preparation of sawdust*

Softwood saw dust, which is collected from a local sawmill (Anatoli, Ioannina, Greece). Sawdust was washed to clean the adhering dirt and impurities, rinsed thoroughly with double distilled water and finally heated in an air oven at 80 ± 100 ^{0}C for 24 h. After drying, the adsorbents were sieved through 0.50-1.00mm sieve and used as such.

5.3.2. Chemicals

The pesticides bromophos methyl (99.1% purity), quinalphos (98.9% purity), pretilachlor (99%) were of residue analysis grade and purchased from Riedel-de Haen (Germany) and CR dye was purchased from Riedel-de Haen (Switzerland) and a stock solution of 2000 mg/L of Congo red was prepared. From the stock solution, various concentrations of working solutions were prepared. The physicochemical properties of the selected compounds presented in section 2.5. All other chemicals, solvents and salts were of the highest purity level supplied by Merck pro-analysis or Lab Scan, Pestiscan.

5.3.3. Characterization

The important properties of the low cost materials used in this study are presented in **Table 5.1**.

Table 5.1. Properties of the adsorbents

Properties	NLP	UTL	SD
Surface area (m2/g)	21.45*	6.50	6.64
Average particle size (nm)	0.054-0.074*	0.710-1.00	0.50-1.00

**Bhattacharyya and Sharma, 2004; Sharma and Bhattacharyya, 2005*

In order to determine the existence of active functional groups on different activated carbons, FTIR (Fourier Transform Infrared Spectroscopy) spectrometer (Shimadzu -8400, Japan) was used at room temperature with pellet (pressed-disk) technique.

Scanning electron microscopy (SEM) pictures of all the adsorbents were taken by Jeol JSM 5600 at 20 kV.

The surface charge (zeta potential) of the adsorbents was measured by Zeta Meter System 3.0 (Zeta-Meter. Inc, USA). The zeta potential was measured 7 times for each pH (3 to 12) and average reading was taken. Between the samples, the cell was flushed with of enough deionised water.

5.3.4. *Experimental procedures*

Batch equilibration method was followed for the optimization process according to the Box-behnken design matrix for all pesticides onto low cost materials that are presented in **Table 5.2** for bromophos methyl, **Table 5.3** for quinalphos and **Table 5.4** for pretilachlor. For congo red, Central Composite Design (CCD) design matrix that are presented in **Table 5.5** for NLP and UTL and for SD **Table 5.6**. For pesticides, 10 ml of pesticides aqueous solution with different pH, initial concentration and adsorbent dose were placed in 15 ml polypropylene centrifuge tube. For congo red, 25 ml of dye solution with different pH, amount of dose and concentrations were placed in 50 ml polypropylene centrifuge tube. The mixture was then shaken at predetermined fixed contact time for specific compounds onto different activated carbons obtained from kinetic study. At the end of the shaking the samples were centrifuged at 4200 rpm for 5 min and the supernatant was collected with a pipette for the determination of compounds concentration.

The removal % was calculated as

$$\text{Removal}\% = 100X\,\frac{(C_0 - C_e)}{C_0} \tag{5.1}$$

where C_0 and C_e are the initial and equilibrium concentrations of specific compounds in the solutions in mg L^{-1} respectively.

Table 5.2: Box-Behnken design matrix, ranges, levels and results for bromophs methyl removal% onto different low cost materials

	Range and Level		
Factors	Low (-1)	Middle (0)	High (+1)
pH	5	7	9
Adsorbent dose (mg/g)	0.2	0.3	0.4
Initial concentration(mg/L)	1	4	7

Run	pH	Dose	Concentration	Removal %					
				NLP		UTL		SD	
				Observed	Predicted	Observed	Predicted	Observed	Predicted
1	-1	+1	0	89.44	90.48	73.63	75.40	71.63	72.03
2	-1	0	+1	70.72	77.61	70.00	66.96	68.00	61.96
3	0	-1	-1	47.84	55.77	56.21	54.94	66.21	60.57
4	+1	-1	0	35.36	34.32	48.93	47.16	56.93	56.53
5(c)	0	0	0	67.60	63.15	86.56	85.00	64.56	62.67
6	+1	0	-1	81.12	74.23	63.90	66.94	59.90	65.94
7	-1	0	-1	82.16	86.97	71.47	75.69	61.47	64.94
8	-1	-1	0	46.80	34.06	58.09	55.13	48.09	50.26
9	0	-1	+1	28.08	33.93	48.78	54.78	38.78	42.65
10	0	+1	-1	92.56	86.71	89.00	83.00	66.00	62.13
11(c)	0	0	0	63.44	63.15	85.32	85.00	63.32	62.67
12	+1	0	+1	53.04	48.23	89.95	85.73	71.95	68.48
13	+1	+1	0	35.36	48.10	90.44	93.40	75.44	73.27
14(c)	0	0	0	58.40	63.15	83.12	85.00	60.12	62.67
15	0	+1	+1	81.12	73.19	91.96	93.23	73.96	79.60

Note: (c) indicates central point

Table 5.3: Box-Behnken design matrix, ranges, levels and results for quinalphos removal% onto different low cost materials

Range and Level			
Factors	Low (-1)	Middle (0)	High (+1)
pH	5	7	9
Adsorbent dose (mg/g)	0.2	0.3	0.4
Initial concentration(mg/L)	1	4	7

Run	pH	Dose	Concentration	Removal %					
				NLP		UTL		SD	
				Observed	Predicted	Observed	Predicted	Observed	Predicted
1	-1	+1	0	80.50	77.51	81.17	79.53	55.52	54.40
2	-1	0	+1	68.11	71.39	69.00	69.86	47.20	47.79
3	0	-1	-1	45.41	45.71	41.00	40.22	28.04	27.51
4	+1	-1	0	27.86	30.85	42.11	43.75	28.80	29.92
5(c)	0	0	0	70.18	68.46	72.52	71.95	49.60	49.21
6	+1	0	-1	69.14	65.86	64.49	63.63	44.11	43.52
7	-1	0	-1	80.50	83.49	69.55	69.46	47.57	47.51
8	-1	-1	0	48.50	45.22	47.12	47.98	32.23	32.82
9	0	-1	+1	34.06	34.06	48.00	46.27	32.83	31.65
10	0	+1	-1	75.20	75.20	74.09	75.82	50.68	51.86
11(c)	0	0	0	68.11	68.46	72.30	71.95	49.45	49.21
12	+1	0	+1	71.21	68.22	80.81	80.90	55.27	55.33
13	+1	+1	0	67.80	71.09	89.83	88.97	61.44	60.85
14(c)	0	0	0	67.08	68.46	71.03	71.95	48.58	49.21
15	0	+1	+1	77.40	77.10	86.67	87.44	59.28	59.81

Note: (c) indicates central point

Table 5.4: Box-Behnken design matrix, ranges, levels and results for pretilachlor removal% onto different low cost materials

	Range and Level		
Factors	Low (-1)	Middle (0)	High (+1)
pH	5	7	9
Adsorbent dose (mg/g)	0.2	0.3	0.4
Initial concentration(mg/L)	1	4	7

Run	pH	Dose	Concentration	Removal %					
				NLP		UTL		SD	
				Observed	Predicted	Observed	Predicted	Observed	Predicted
1	-1	+1	0	78.00	76.56	71.63	75.45	65.54	71.72
2	-1	0	+1	66.00	66.56	67.00	65.81	55.72	52.66
3	0	-1	-1	44.00	43.13	46.21	48.84	33.11	36.23
4	+1	-1	0	27.00	28.44	48.13	44.31	64.00	57.83
5(c)	0	0	0	68.00	66.33	79.56	79.67	58.56	57.43
6	+1	0	-1	67.00	66.44	61.90	63.09	52.08	55.13
7	-1	0	-1	78.00	81.19	73.47	73.04	56.16	52.34
8	-1	-1	0	47.00	44.69	52.09	49.88	38.05	38.75
9	0	-1	+1	33.00	34.75	43.78	47.18	38.76	41.12
10	0	+1	-1	84.50	82.75	79.00	75.60	59.83	57.47
11(c)	0	0	0	66.00	66.33	78.32	79.67	58.38	57.43
12	+1	0	+1	69.00	65.81	82.95	83.38	65.25	69.08
13	+1	+1	0	75.00	77.31	86.44	88.65	72.54	71.84
14(c)	0	0	0	65.00	66.33	81.12	79.67	55.36	57.43
15	0	+1	+1	75.00	75.88	92.96	90.33	69.99	66.86

Note: (c) indicates central point

Table 5.5. Central composite design(CCD) matrix for congo red removal onto different low cost materials

Range and Level					
Factors	*-α*	*-1(Low)*	*0 (Middle)*	*+1(High)*	*+α*
pH	2.64	4	6	8	9.36
Dose (g)	0.13	0.20	0.30	0.40	0.47
Concentration (mg L^{-1})	7.96	25	50	75	92.04

				Removal %			
Run	*pH*	*Dose*	*Concentration*	NLP		UTL	
				Observed	*predicted*	*Observed*	*predicted*
1	-1	-1	1	90.84	90.10	88.22	91.25
2	-1	1	1	95.60	98.22	91.87	94.93
3	-1	-1	-1	77.88	78.63	74.66	74.36
4	0	-α	0	82.01	82.84	81.59	82.27
5	+α	0	0	86.07	87.22	92.33	95.99
6	0	0	+α	93.23	91.84	90.54	87.23
7	1	-1	-1	90.49	87.62	87.88	85.04
8	1	-1	1	84.92	86.18	82.47	81.61
9(c)	0	0	0	92.67	92.23	90.00	90.47
10(c)	0	0	0	90.01	92.23	87.41	90.47
11(c)	0	0	0	93.28	92.23	90.59	90.47
12(c)	0	0	0	95.27	92.23	92.52	90.47
13(c)	0	0	0	92.49	92.23	89.82	90.47
14(c)	0	0	0	89.70	92.23	92.45	90.47
15	0	+α	0	94.23	93.76	87.63	86.63
16	-α	0	0	91.31	90.52	92.56	88.58
17	0	0	-α	86.49	88.24	64.57	67.56
18	1	1	-1	92.00	92.49	89.35	86.55
19	1	1	1	86.29	85.29	92.54	93.06
20	-1	1	-1	94.01	92.50	67.02	68.10

Note: (c) indicates central point

Table 5.6a. Full factorial design for screening of factors for congo red removal onto SD

Factors	Range and levels		
Coded values	-1 (Low)	0 (Middlie)	+1 (High)
pH	3	6	9
Concentration (mg/L)	25	50	75
Dose (g)	0.1	0.3	0.5
Contact time (hour)	1	2	3

Run	pH	Concentration	Dose	Contact Time	Removal %
1	-1	1	1	-1	68.43
2	1	-1	1	1	91.41
3(c)	0	0	0	0	80.66
4	1	-1	-1	-1	40.98
5	1	-1	0	1	42.75
6	1	1	1	1	93.18
7	1	1	1	-1	87.57
8	-1	1	1	1	85.03
9(c)	0	0	0	0	82.88
10	-1	1	-1	1	42.83
11	0	0	0	0	82.65
12	-1	-1	-1	1	43.20
13	1	1	-1	-1	31.56
14	-1	-1	1	-1	77.57
15	-1	-1	1	1	81.90
16	1	-1	1	-1	86.65
17	-1	-1	-1	-1	29.25
18	-1	1	-1	-1	28.90
19	1	1	-1	1	54.49

Note: (c) indicates central point

Table 5.6b. Central composite design(CCD) matrix for congo red removal onto SD

Factors	*Range and Level*				
Coded value	*-α*	*-1(Low)*	*0 (Middle)*	*+1(High)*	*+α*
Dose (g)	0.65	0.75	1.0	1.25	1.35
Contact time (hour)	3.59	4	5	6	6.41

Run	*Dose*	Contact time	*Removal %*	
			Observed	*predicted*
1	+*α*	0	90.87	90.47
2	0	+*α*	95.73	94.62
3	1	-1	88.10	89.71
4	-1	-1	71.42	75.47
5(c)	0	0	95.46	92.74
6	-*α*	0	81.56	77.72
7(c)	0	0	92.62	92.74
8(c)	0	0	91.87	92.74
9	0	-*α*	86.54	83.41
10(c)	0	0	93.23	92.74
11	1	1	92.23	92.42
12	-1	1	86.00	88.62
13(c)	0	0	90.54	92.74

Note: (c) indicates central point

5.3.5. *Extraction and analysis of compounds*

For residue analysis of all pesticides, 5 ml of supernatant, each after adsorption and desorption, was extracted twice with 2.5 ml n-hexane using a vortex for 1 min. In the combined extracts a small amount of anhydrous Na_2SO_4 was added to remove residual water. The acetone desorption phase was filtered through glass wool fiber, containing anhydrous Na_2SO_4 as a part of clean up procedure for the samples. An aliquot of 1.0 μL of the *n*-hexane and acetone extract was injected into a Shimadzu 14B gas chromatograph equipped with ^{63}Ni electron capture detector (ECD) at 300^0 C. A DB 1 column (J & W Scientific, Folsom, CA, USA), 30 m of length, 0.32 mm i.d., coated with dimethylpolysiloxane of a film thickness of 0.25 µm was used. The temperature program was: from 80 ^{0}C (2 min) to 290^0 (10 min) at 21^{0}C min^{-1}. Injector temperature was set to 250 ^{0}C and the injector mode was splitless. Helium and nitrogen was used as the carrier (1.5 mL min^{-1}) and the make-up (35 mL min^{-1}) gases, respectively. Under these conditions, retention times of bromophos methyl, quinalphos and pretilachlor were 11.10, 11.40 and 13.30 minutes respectively. The recovery obtained with the extraction method used was greater than 90% for all pesticides investigated.

Calibration curve of congo red was prepared by measuring absorbance of different predetermined concentrations of the samples at λ_{max} 496 nm using UV–vis spectrophotometer (Jasco, V-530, Japan).

5.4. Results and discussion

5.4.1. *FTIR analyses of adsorbents*

5.4.1.1. Neem leaves powder

FTIR measurements showed the presence of a large number of active functional groups on neem leaves powder **(Figure 5.1)**, OH ((3597–3600cm–1), COOH (3297 cm^{-1}) , C O (1633 -1688 cm^{-1}), >C-C< (1656cm^{-1}), the band at 1105cm^{-1} represented the C-S group (thiocarbonyl), etc., in Neem leaves and these groups may contribute to the excellent sorption properties of NLP.

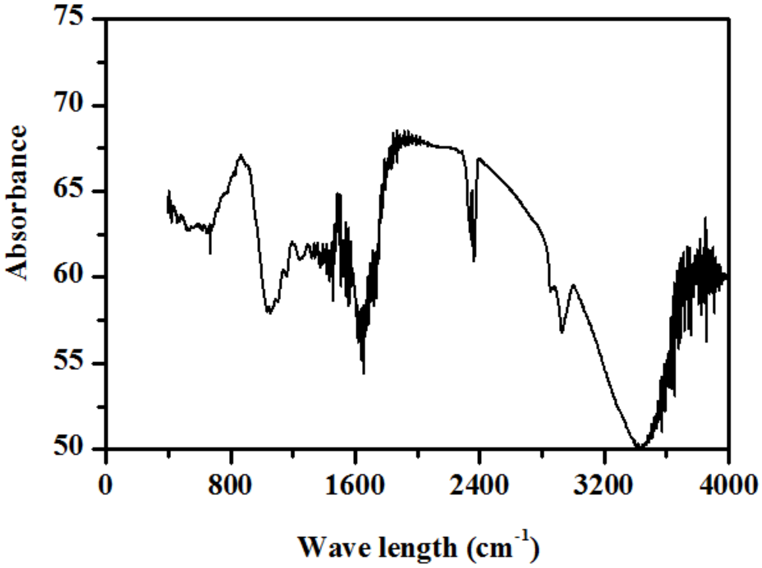


Figure 5.1. FTIR- spectra of NLP.

5.4.1.2. Used tea leaves

The FTIR (Fourier transform infrared spectroscopy) analysis showed various functional groups observed on the surface of used tea leaves **(Figure 5.2)**. Among these, a strong sharp peak in the region of 1660-1730 cm^{-1} indicates the presence of C=O (carboxylic acids) group and the peak at 1300-1400 cm^{-1} related to N=O (nitro compounds). The peak at 2850- 3000 cm^{-1} corresponds to C-H (alkanes) groups. The broad peak at 3100-3600cm^{-1} indicates the presence of alcohol and phenol compound that represent the H-bonded O-H Stretch.

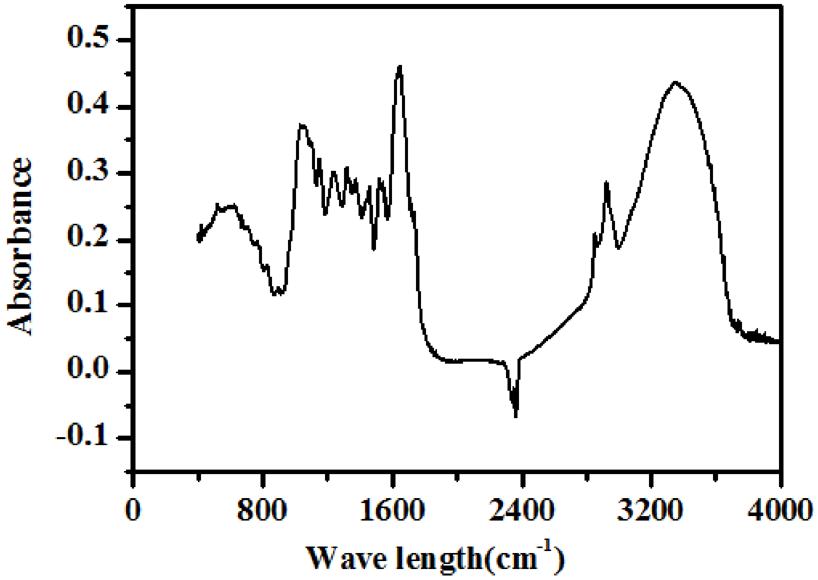


Figure 5.2. FTIR- spectra of used tea leaves.

5.4.1.3. Sawdust

The FTIR spectra were recorded in the region 400– 4000 cm^{-1}. An FTIR spectrum of sawdust is shown in **Figure 5.3**. The strong band at 3360 cm^{-1} is due to -OH stretching. The band at 1624 cm^{-1} is attributed C=O (carboxylic) bending. The stretching vibration at 1750 cm^{-1} also responsible for C=O band. The band at 2356 cm^{-1} is attributed to -OH stretching. The strong broad stretching of O-H (acids) also observed at 2500-3300cm^{-1}. The bands at 2928 cm^{-1} corresponds to symmetric and asymmetric stretching vibration of -CH2 group (alkane). The stretching vibrations of **Si-H** (silicon) functional groups attributed at 2100-2360 cm^{-1}. A strong bending vibration of =C-H & =CH_2 was also shown at 880-995 cm^{-1}

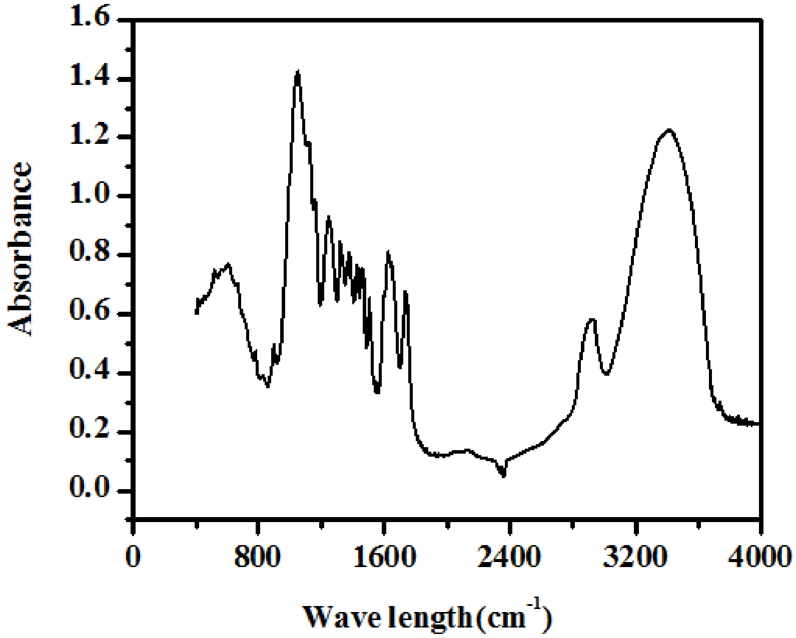


Figure 5.3. FTIR- spectra of sawdust.

5.4.2. *SEM analyses of adsorbents*

The Scanning electron microscopy (SEM) pictures for NLP **(Figure 5.4)**, UTL **(Figure 5.5)**, and SD **(Figure 5.6)** clearly reveals the porous nature of the surface that was enough responsible for selected pesticides and dye adsorption.

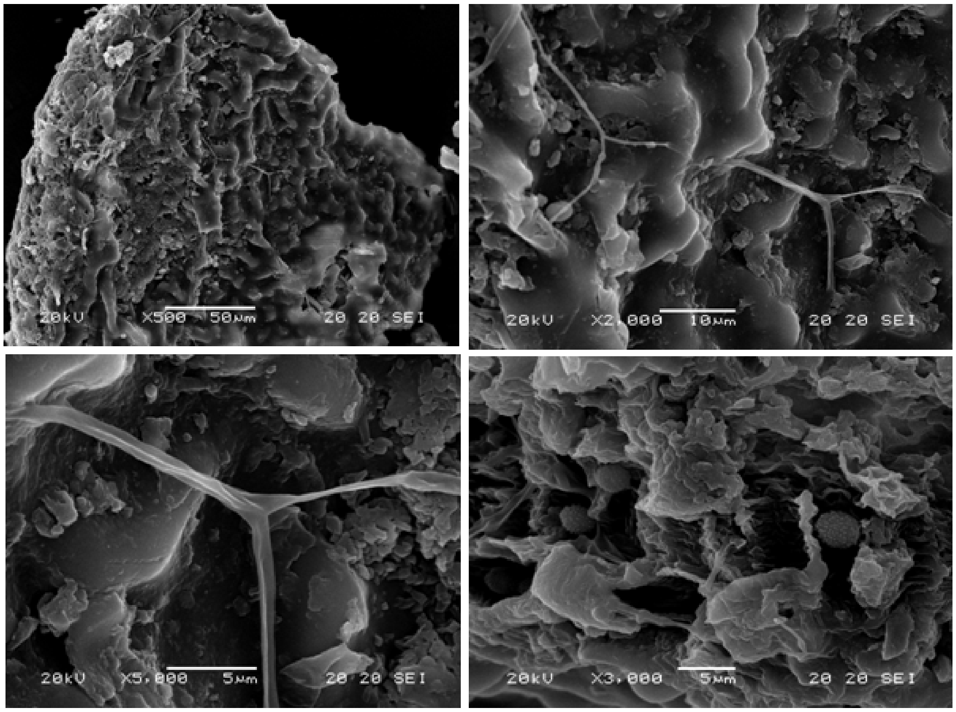


Figure 5.4. SEM pictures of NLP

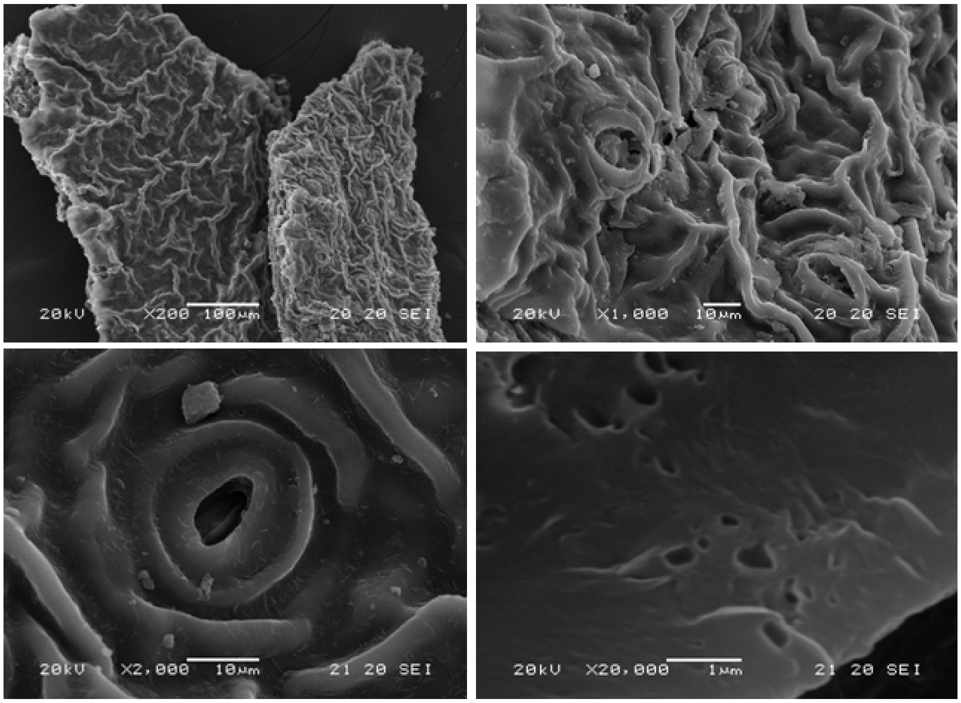


Figure 5.5. SEM pictures of UTL

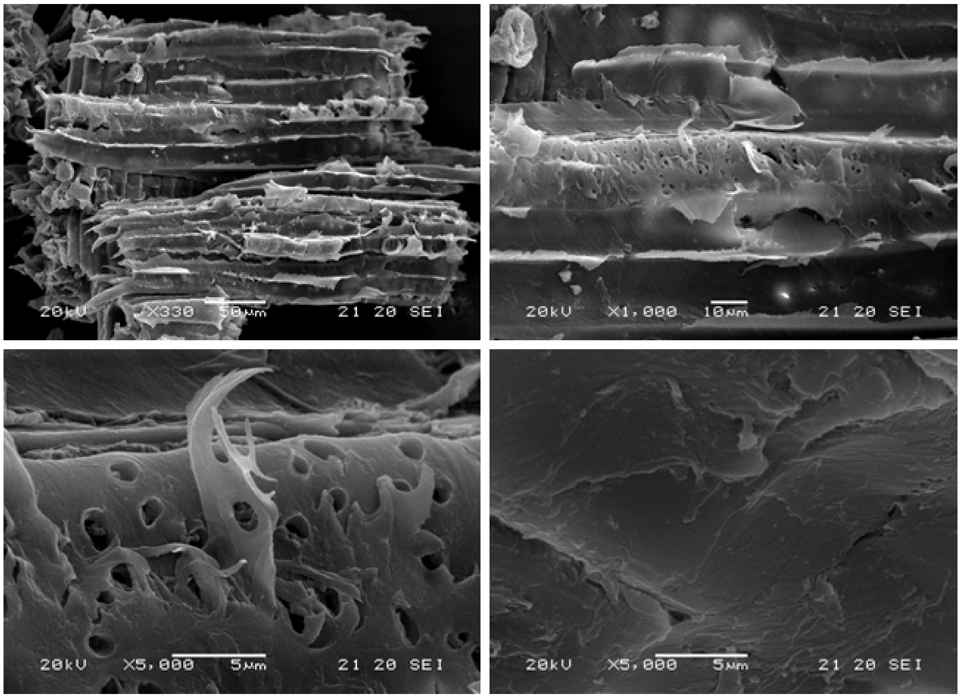


Figure 5.6. SEM pictures of SD

5.4.3. *Effect of contact time*

It may be seen from **Figure 5.7**, that the percentage adsorption for all compounds increases with an increase in the contact time and attains equilibrium after some time onto NLP. For instances, it has been seen from the **Figure 5.7** that all the pesticides reached its equilibrium at 300 minutes, but congo red took more time in order to reach the equilibrium. CR is a large molecule having molecular weight of 696.66 g/mol causes to slower rate to reach equilibrium. It is also noted that all the compounds removed by NLP more than 85% within 240min. After this equilibrium points, no more removal percentage was observed for all compounds. Therefore, contact time of 300min was selected for all pesticides whereas 360 min for CR , for further study.

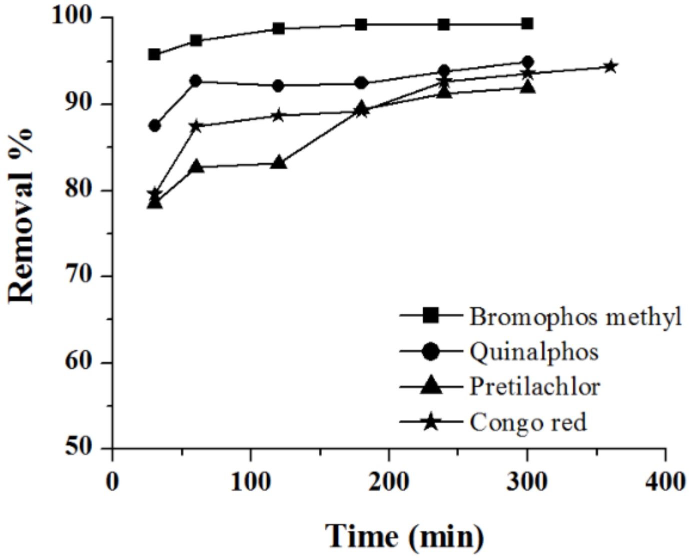


Figure 5.7. Effect of contact time for the removal of bromophos methyl, quinalphos, pretilachlor and congo red onto NLP (dosage = 0.3g/10ml in Deionised (DI) water, Concentration = 10 mg/l, for pesticides and dosage= 0.3 g/25ml in DI water, Concentration =50 mg/L for congo red

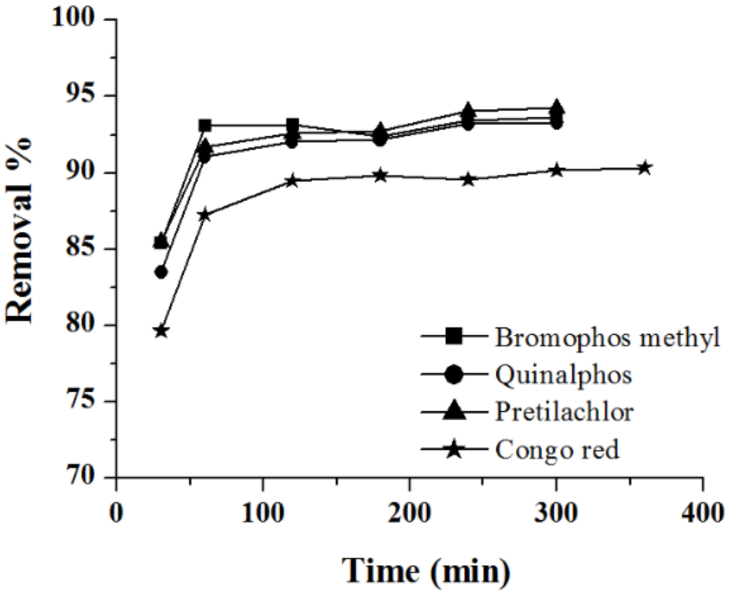


Figure 5.8. Effect of contact time for the removal of bromophos methyl, quinalphos, pretilachlor and congo red onto UTL (dosage = 0.3g/10ml in DI water, Concentration = 10 mg/l, for pesticides and dosage= 0.3 g/25ml in DI water, Concentration =50 mg/L for congo red

Figure 5.8 indicate the effect of contact time on percentage removal of selected compounds onto UTL. The removal% is observed to increase with increasing contact time. For the first 60 min contact time, 0.3 g of UTL removed more than 87% from the solutions and it gradually increased with increasing contact time and finally adsorbed more than 90% for all pesticides at 300 min and reached the equilibrium. But congo red has taken more time (about 360 min) in order to reached its equilibrium due to its large molecular structure.

Figure 5.9 represented the influence of contact time for the removal of different selected compounds onto SD. The removal increased 58.93–87.78%, 50.60–75.54%, 57.85–79.14% and 43.05–86.32% for bromophos methyl, quinalphos, pretilachlor and congo red with an increase in contact time (1–10h, 1-8h for CR) and became almost constant after 10h for pesticides and 8h for CR. Since the uptake of the dye at the active sites of adsorbent is a rapid process and initially CR adsorbed at higher rate and gradually surface is covered by the large molecules of CR and slowdown rapidly after certain time.

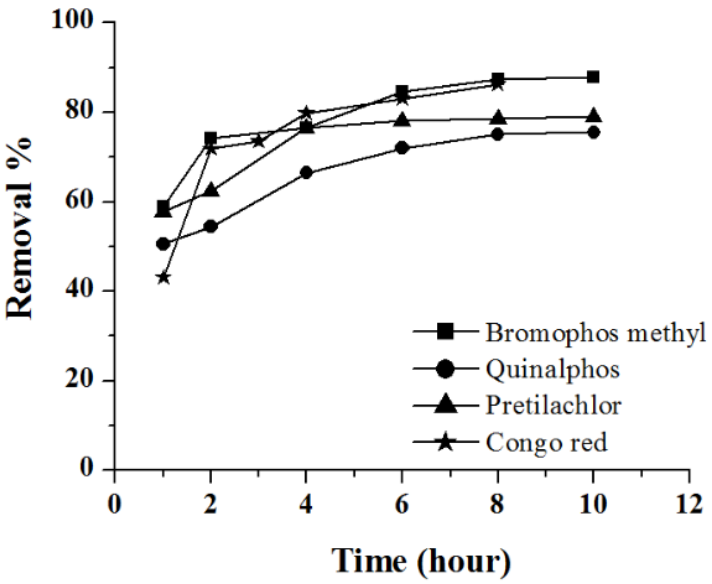


Figure 5.9. Effect of contact time for the removal of bromophos methyl, quinalphos, pretilachlor and congo red onto SD (dosage = 0.3g/10ml in DI water, Concentration = 10 mg/l, for pesticides and dosage= 0.3 g/25ml in DI water, Concentration =50 mg/L for congo red

5.4.4. *Kinetic study*

Two widely used kinetic models were applied in this study in order to analyze kinetic data. The parameters were the same as mentioned earlier for effect of contact time study. Lagergren pseudo first order model can be represented by following the equation (5.2)

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1 t}{2.303} \tag{5.2}$$

The pseudo second order can be expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{5.3}$$

where q_e the amount of compounds adsorbed onto adsorbents at equilibrium (mg g^{-1}) and q_t is the amount (mg g^{-1}) of compounds adsorbed at any time t (min) and K_1 and K_2 are the rate constants of pseudo first order and second order model respectively.

The two models were developed by constructing linear plot of log ($q_e - q_t$) vs. t for pseudo first order and t/q_t vs. t for pseudo second order model. The rate constants K_1, K_2 measured from the slopes of corresponding linear plots. According to the regression coefficient, the adsorption of all selected compounds onto different low cost materials is best described by the pseudo second order kinetic model than pseudo first order (**Table 5.6**). Besides, the calculated q_e values for pseudo second order kinetic model is similar to experimental q_e value indicating the best fitted model **(Figure 5.10, 5.11, 5.12)** than pseudo first order model. Hameed (2009) also found the similar results for removal of dye onto spent tea leaves. Neem leaves powder also showed the same behaviour towards the removal of congo red (Bhattacharyya and Sharma, 2004).

Table 5.7. A comparison of the pseudo first order rate constants and pseudo second order rate constant with calculated (q_e-cal) and experimental (q_e-exp) values obtained at single initial concentration

Adsorbents	Compounds	$q_{e,}$ exp	Kinetic model					
			Pseudo-first order			Pseudo-second order		
			K_1	$q_{e,}$ cal.	R^2	K_2	$q_{e,}$ cal.	R^2
NLP	Bromophos methyl	0.286	0.015	0.153	0.921	2.644	0.287	0.999
	Quinalphos	0.278	0.007	0.172	0.659	1.131	0.279	0.999
	Pretilachlor	0.245	0.005	0.149	0.961	1.124	0.247	0.999
	Congo red	3.869	0.010	0.874	0.920	0.084	3.932	0.999
UTL	Bromophos methyl	0.289	0.011	0.141	0.458	1.705	0.298	0.999
	Quinalphos	0.250	0.018	0.225	0.865	1.273	0.252	0.999
	Pretilachlor	0.265	0.014	0.212	0.864	1.171	0.267	0.999
	Congo red	3.703	0.012	0.609	0.828	0.084	3.703	1.000
SD	Bromophos methyl	0.271	0.552	0.473	0.923	5.555	0.287	0.999
	Quinalphos	0.209	0.545	0.459	0.943	5.328	0.226	0.998
	Pretilachlor	0.244	0.566	0.392	0.964	7.881	0.257	0.999
	Congo red	3.795	0.485	1.438	0.937	0.237	4.282	0.995

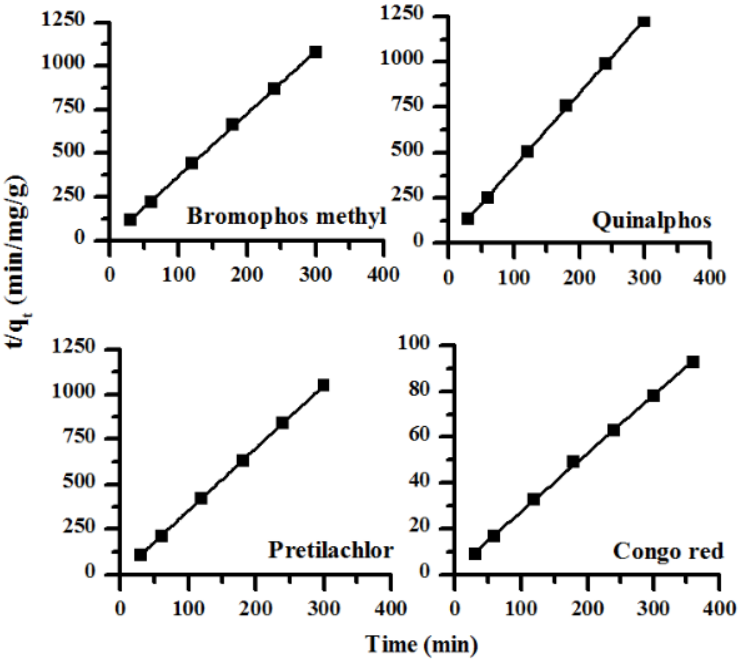


Figure 5.10. Pseudo second order kinetic plot for NLP, where adsorbent dosage = 0.3g/10ml in DI water, Concentration = 10 mg/l, for pesticides and dosage= 0.3 g/25ml in DI water, Concentration =50 mg/L for congo red

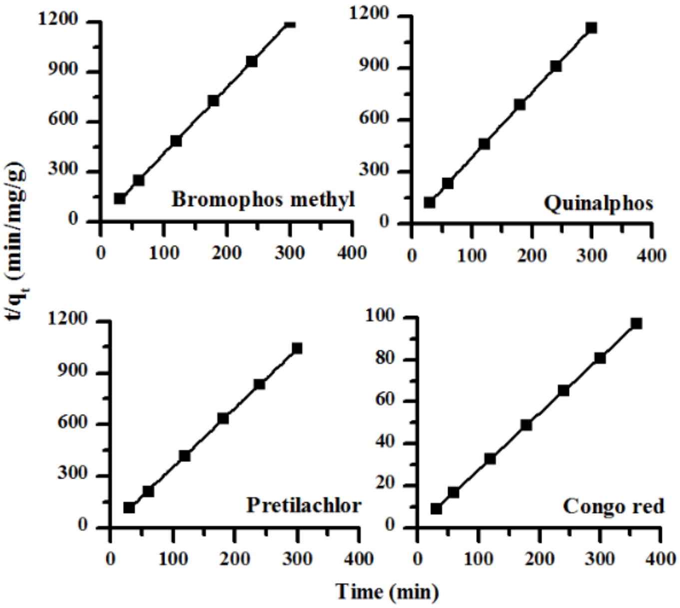


Figure 5.11. Pseudo second order kinetic plot for UTL, where dosage = 0.3g/10ml in DI water, Concentration = 10 mg/l, for pesticides and dosage= 0.3 g/25ml in DI water, Concentration =50 mg/L for congo red

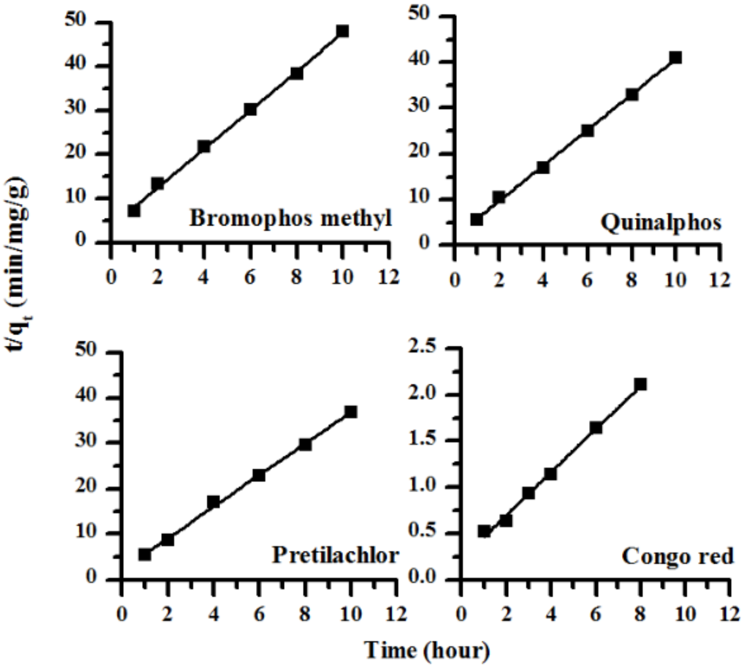


Figure 5.12. Pseudo second order kinetic plot for SD, where dosage = 0.3g/10ml in DI water, Concentration = 10 mg/l, for pesticides and dosage= 0.3 g/25ml in DI water, Concentration =50 mg/L for congo red

5.4.5. *Statistical analysis based on response surface methodology*

In this study, Box-Behnken design was used as RSM for the treatments of three factors pH, dose and concentration for pesticides. **Table 5.2** (for bromophos methyl), **Table 5.**3 (for quinalphos) and **Table 5.4** (for pretilachlor), represents the experimental parameters and levels used by Box-Behnken design model for NLP, UTL and SD respectively. The corresponding design matrix consisted of 15 experiments including three center points.

Central Composite Design (CCD) was used for the removal CR by NLP and UTL, the CCD design matrix are presented in **Table 5.5**. In the present study, the three factors CCD with two levels experimental (2^3) design model, containing 8 factorial points, 6 axial points and 6 replicates at the center points were employed, indicating that altogether 20 experiments were required (($N=2^n +2n+n_c=2^3 +2*3+6=20$), where N is the total number of experiments required, *n* is the number of factors and n_c is the center points). The center points are used to determine the experimental error and the replication of the data. The pH, adsorbent dose and initial concentration were the input factors in order to get the highest removal % of CR onto different selected activated carbons. In this study, α value was fixed at 1.682 (rotatable).

Table 5.8. ANOVA for full factorial design of congo red removal onto saw dusts

Source	**Sum of Squares**	**df**	**Mean Square**	**F- Value**	**Prob > F**
Curvature.	1057.24	1	1057.24	709.45	0.00
(1)pH	319.34	1	319.34	214.29	0.00
(2)Concentration	0.18	1	0.18	0.12	0.76
(3)Dose	8000.41	1	8000.41	5368.56	0.00
(4)Contact Time	439.74	1	439.74	295.08	0.00
1 by 2	8.61	1	8.61	5.78	0.14
1 by 3	25.70	1	25.70	17.25	0.05
1 by 4	11.80	1	11.80	7.92	0.11
2 by 3	1.51	1	1.51	1.02	0.42
2 by 4	73.36	1	73.36	49.23	0.02
3 by 4	28.30	1	28.30	18.99	0.04
Lack of Fit	81.80	5	16.36	10.98	0.09
Pure Error	2.98	2	1.49		
Total SS	10050.99	18			

For removal of CR by sawdust, another efficient approach of statistical design of experiments was adopted in order to check the suitability of different methodological application. At first, three-level full factorial design with four factors was used in order to eliminate unimportant factors (screening test) before investing time and money in a more elaborate experiment. For this, 16 combinations of all factors and three center points, total 19 experimental runs were carried out **(Table 5.6a).** Four factors: pH, concentration, dose and contact time were chosen, according to review of literature. From the analysis of data **(Table 5.8)** it can be seen that pH, adsorbent dose and contact time have significant impact ($p < 0.05$) on CR removal by sawdust. But none of interactions of pH with other factors were not significant and finally adsorbent dose and contact time was chosen for further study. The curvature was also significant, indicating that a higher order model or response surface study is needed in order to uncover the behavior of the significant factors. In order to evaluate the broader effects of the two significant selected factors (adsorbent dose and contact time) obtained from the screening test, a central composite design (CCD) was used as a response surface technique. The applied central composite design was consisted of 13 experiments including 5 central points. The design matrix is depicted in **Table 5.6b**.

STATISTICA® statistical software was used for the design of experiment. A second order polynomial model used to fit the response to the independent variables is shown:

$$y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \qquad (5.4)$$

where y is the percentage of compounds removal, β_0 the intercept and $\beta_{i,}$ $\beta_{ii},$ β_{ij} are the coefficients of parameters for linear, squared and interaction factor effects respectively.

Table 5.9. ANOVA for Response Surface Quadratic Model for bromophos methyl, quinalphos and pretilachlor onto NLP

Bromophos methyl

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	890.92	2	445.46	21.01	0.05
(2)Dose(L+Q)	2862.16	2	1431.08	67.50	0.01
(3)Initial concentration(L+Q)	968.00	2	484.00	22.83	0.04
1*2	454.54	1	454.54	21.44	0.04
1*3	69.22	1	69.22	3.26	0.21
2*3	17.31	1	17.31	0.82	0.46
Lack of Fit	662.21	3	220.74	10.41	0.09
Pure Error	42.40	2	21.20		
Correction Total	6027.99	14			

R^2=0.883; Adjusted R^2=0.673; L indicated linear effect; Q indicated quadratic effect

Quinalphos

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	219.69	2	109.84	44.20	0.02
(2)Dose(L+Q)	3279.46	2	1639.73	659.84	0.00
(3)Initial concentration(L+Q)	76.72	2	38.36	15.44	0.06
1*2	15.78	1	15.78	6.35	0.13
1*3	52.19	1	52.19	21.00	0.04
2*3	45.89	1	45.89	18.47	0.05
Lack of Fit	78.98	3	26.33	10.59	0.09
Pure Error	4.97	2	2.49		
Correction Total	3806.54	14			

R^2=0.977; Adjusted R^2=0.938; L indicated linear effect; Q indicated quadratic effect

Pretilachlor

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	121.67	2	60.83	26.07	0.04
(2)Dose(L+Q)	3646.63	2	1823.31	781.42	0.00
(3)Initial concentration(L+Q)	149.98	2	74.99	32.14	0.03
1*2	72.25	1	72.25	30.96	0.03
1*3	49.00	1	49.00	21.00	0.04
2*3	0.56	1	0.56	0.24	0.67
Lack of Fit	43.44	3	14.48	6.21	0.14
Pure Error	4.67	2	2.33		
Correction Total	4111.83	14			

R^2=0.988; Adjusted R^2=0.967; L indicated linear effect; Q indicated quadratic effect

Table 5.10. ANOVA for Response Surface Quadratic Model for bromophos methyl, quinalphos and pretilachlor onto UTL

Bromophos methyl

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	254.67	2	127.34	41.95	0.02
(2)Dose(L+Q)	2565.31	2	1282.66	422.59	0.00
(3)Initial concentration(L+Q)	101.85	2	50.93	16.78	0.06
1*2	168.61	1	168.61	55.55	0.02
1*3	189.34	1	189.34	62.38	0.02
2*3	26.99	1	26.99	8.89	0.10
Lack of Fit	153.03	3	51.01	16.81	0.06
Pure Error	6.07	2	3.04		
Correction Total	3399.56	14			

R^2=0.953; Adjusted R^2=0.868; L indicated linear effect; Q indicated quadratic effect

Quinalphos

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	15.97	2	7.99	12.35	0.07
(2)Dose(L+Q)	3165.78	2	1582.89	2446.88	0.00
(3)Initial concentration(L+Q)	168.20	2	84.10	130.00	0.01
1*2	46.72	1	46.72	72.22	0.01
1*3	71.15	1	71.15	109.98	0.01
2*3	7.78	1	7.78	12.03	0.07
Lack of Fit	15.54	3	5.18	8.01	0.11
Pure Error	1.29	2	0.65		
Correction Total	3491.75	14			

R^2=0.995; Adjusted R^2=0.986; L indicated linear effect; Q indicated quadratic effect

Pretilachlor

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	108.00	2	54.00	27.43	0.04
(2)Dose(L+Q)	2848.33	2	1424.16	723.46	0.00
(3)Initial concentration(L+Q)	136.06	2	68.03	34.56	0.03
1*2	88.08	1	88.08	44.74	0.02
1*3	189.34	1	189.34	96.18	0.01
2*3	67.16	1	67.16	34.12	0.03
Lack of Fit	79.12	3	26.37	13.40	0.07
Pure Error	3.94	2	1.97		
Correction Total	3470.26	14			

R^2=0.976; Adjusted R^2=0.932; L indicated linear effect; Q indicated quadratic effect

Table 5.11. ANOVA for Response Surface Quadratic Model for bromophos methyl, quinalphos and pretilachlor onto SD

Bromophos methyl

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	46.50	2	23.25	4.43	0.18
(2)Dose(L+Q)	754.40	2	377.20	71.87	0.01
(3)Initial concentration(L+Q)	0.81	2	0.41	0.08	0.93
1*2	6.33	1	6.33	1.21	0.39
1*3	7.62	1	7.62	1.45	0.35
2*3	313.11	1	313.11	59.66	0.02
Lack of Fit	200.43	3	66.81	12.73	0.07
Pure Error	10.50	2	5.25		
Correction Total	1342.18	14			

R^2=0.843; Adjusted R^2=0.559; L indicated linear effect; Q indicated quadratic effect

Quinalphos

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	7.47	2	3.74	12.35	0.07
(2)Dose(L+Q)	1481.13	2	740.56	2446.88	0.00
(3)Initial concentration(L+Q)	78.69	2	39.35	130.00	0.01
1*2	21.86	1	21.86	72.22	0.01
1*3	33.29	1	33.29	109.98	0.01
2*3	3.64	1	3.64	12.03	0.07
Lack of Fit	7.27	3	2.42	8.01	0.11
Pure Error	0.61	2	0.30		
Correction Total	1633.64	14			

R^2=0.995; Adjusted R^2=0.986; L indicated linear effect; Q indicated quadratic effect

Pretilachlor

Source	**Sum of Squares**	**df**	**Mean Square**	**F-Value**	**Prob > F**
(1) pH (L+Q)	267.31	2	133.65	41.24	0.02
(2)Dose(L+Q)	1120.84	2	560.42	172.92	0.01
(3)Initial concentration(L+Q)	189.50	2	94.75	29.24	0.03
1*2	89.88	1	89.88	27.73	0.03
1*3	46.39	1	46.39	14.31	0.06
2*3	5.08	1	5.08	1.57	0.34
Lack of Fit	155.74	3	51.91	16.02	0.06
Pure Error	6.48	2	3.24		
Correction Total	1895.48	14			

R^2=0.914; Adjusted R^2=0.760; L indicated linear effect; Q indicated quadratic effect

Table 5.12. ANOVA for Response Surface Quadratic Model for congo red onto diffrent NLP and UTL

NLP					
Source	**Sum of Squares**	**df**	**Mean Square**	**F- Value**	**Prob > F**
(1)pH (L)	13.21	1	13.21	3.01	0.14
pH (Q)	20.29	1	20.29	4.62	0.08
(2)Dose (L)	143.86	1	143.86	32.75	0.00
Dose (Q)	27.73	1	27.73	6.31	0.05
(3)Concentration(L)	15.61	1	15.61	3.55	0.12
Concentration(Q)	8.63	1	8.63	1.96	0.22
1L by 2L	40.54	1	40.54	9.23	0.03
1L by 3L	83.44	1	83.44	19.00	0.01
2L by 3L	16.59	1	16.59	3.78	0.11
Lack of Fit	29.15	5	5.83	1.33	0.38
Pure Error	21.96	5	4.39		
Correction total	412.41	19			

R^2=0.876; Adjusted R^2=0.764; L indicated linear effect; Q indicated quadratic effect

UTL					
Source	**Sum of Squares**	**df**	**Mean Square**	**F- Value**	**Prob > F**
(1)pH (L)	66.27	1	66.27	18.26	0.01
pH (Q)	5.92	1	5.92	1.63	0.26
(2)Dose (L)	22.96	1	22.96	6.33	0.05
Dose (Q)	65.32	1	65.32	18.00	0.01
(3)Concentration(L)	467.06	1	467.06	128.71	0.00
Concentration(Q)	308.04	1	308.04	84.89	0.00
1L by 2L	30.15	1	30.15	8.31	0.03
1L by 3L	206.35	1	206.35	56.86	0.00
2L by 3L	49.45	1	49.45	13.63	0.01
Lack of Fit	87.24	5	17.45	4.81	0.05
Pure Error	18.14	5	3.63		
Correction total	1319.22	19			

R^2=0.920; Adjusted R^2=0.848; L indicated linear effect; Q indicated quadratic effect

The sufficiency of the model was evaluated through analysis of variance (ANOVA). The ANOVA for the response surface quadratic model with two way interactions for all selected pesticides removal% onto NLP is depicted in **Table 5.9,** onto UTL in **Table 5.10** and SD in **Table 5.11.** The model "regression coefficient (R^2) " indicating the percentage of the variability can be revealed by the model. The Lack of Fit (LOF) is the variation of the data around the fitted model. LOF is a special investigative test for adequacy of a model fit, because the effects of the additional higher-order terms are removed from the error. In this study, central points are used for calculating the pure error. If the model does not fit the data well, this will be significant. In our present study with regards to removal% onto different adsorbents, the LOF is not significant for all case relative to the pure error, indicating good response to the model.

Table 5.13. ANOVA for Response Surface Quadratic Model for congo red onto saw dusts

Source	**Sum of Squares**	**df**	**Mean Square**	**F- Value**	**Prob > F**
(1)Dose (L)	162.69	1	162.69	49.11	0.00
Dose (Q)	130.06	1	130.06	39.26	0.00
(2)Contact time (L)	125.66	1	125.66	37.94	0.00
Contact time (Q)	24.17	1	24.17	7.30	0.05
1L by 2L	27.30	1	27.30	8.24	0.05
Lack of Fit	51.86	3	17.29	5.22	0.07
Pure Error	13.25	4	3.31		
Correction total	522.78	12			

R^2=0.875; Adjusted R^2=0.786; L indicated linear effect; Q indicated quadratic effect

The ANOVA for the response surface quadratic model with two way interactions for CR removal% onto NLP and UTL is depicted in **Table 5.12,** and ANOVA for CR removal by sawdust is presented in **Table 5.13.**

5.4.6. *Standardized Pareto chart*

A Pareto Chart is a vertical bar graph showing factors importance in a prioritized order, so it can be determined which factor should be tackled first. In order to perceive the importance of different actual factors and their interactions Standardized Pareto chart are developed by the software that are represented in **Figure. 5.13** for selected compounds removal by NLP, **Figure 5.14** by UTL and **Figure 5.15** for SD according to the rank. The vertical line which overpass through the standardized factors determine the statistical significance at 95% confidence intervals. The sign + and – reflects the positive and negative effect of the corresponding factors respectively. Positive coefficients indicate the removal is favored and negative coefficients indicate unfavorable for removal by the factors and their interactions.

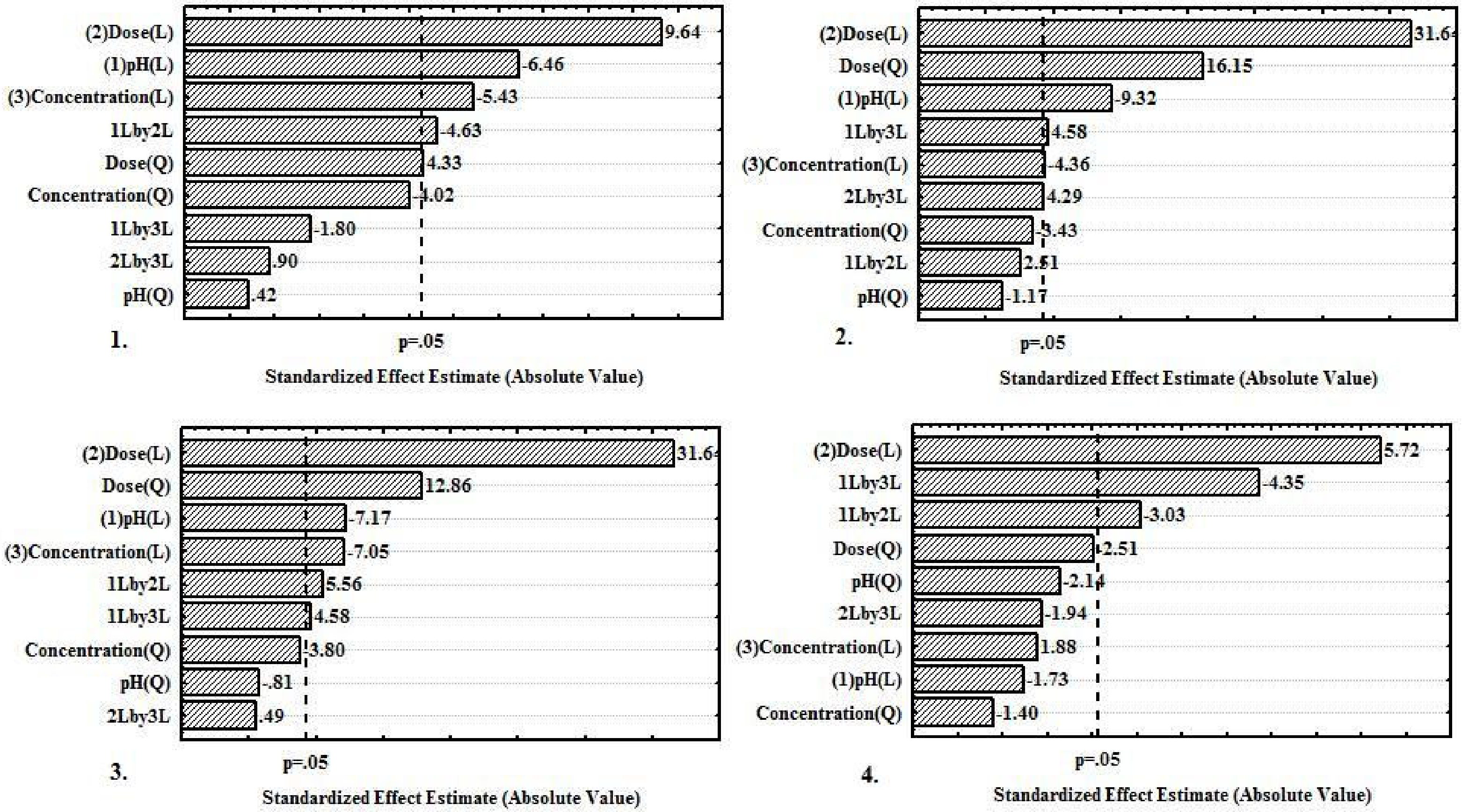


Figure 5.13. Standardized Pareto chart for main and interaction factors of 1.bromophos methyl, 2. quinalphos, 3. pretilachlor and 4. CR removal by NLP

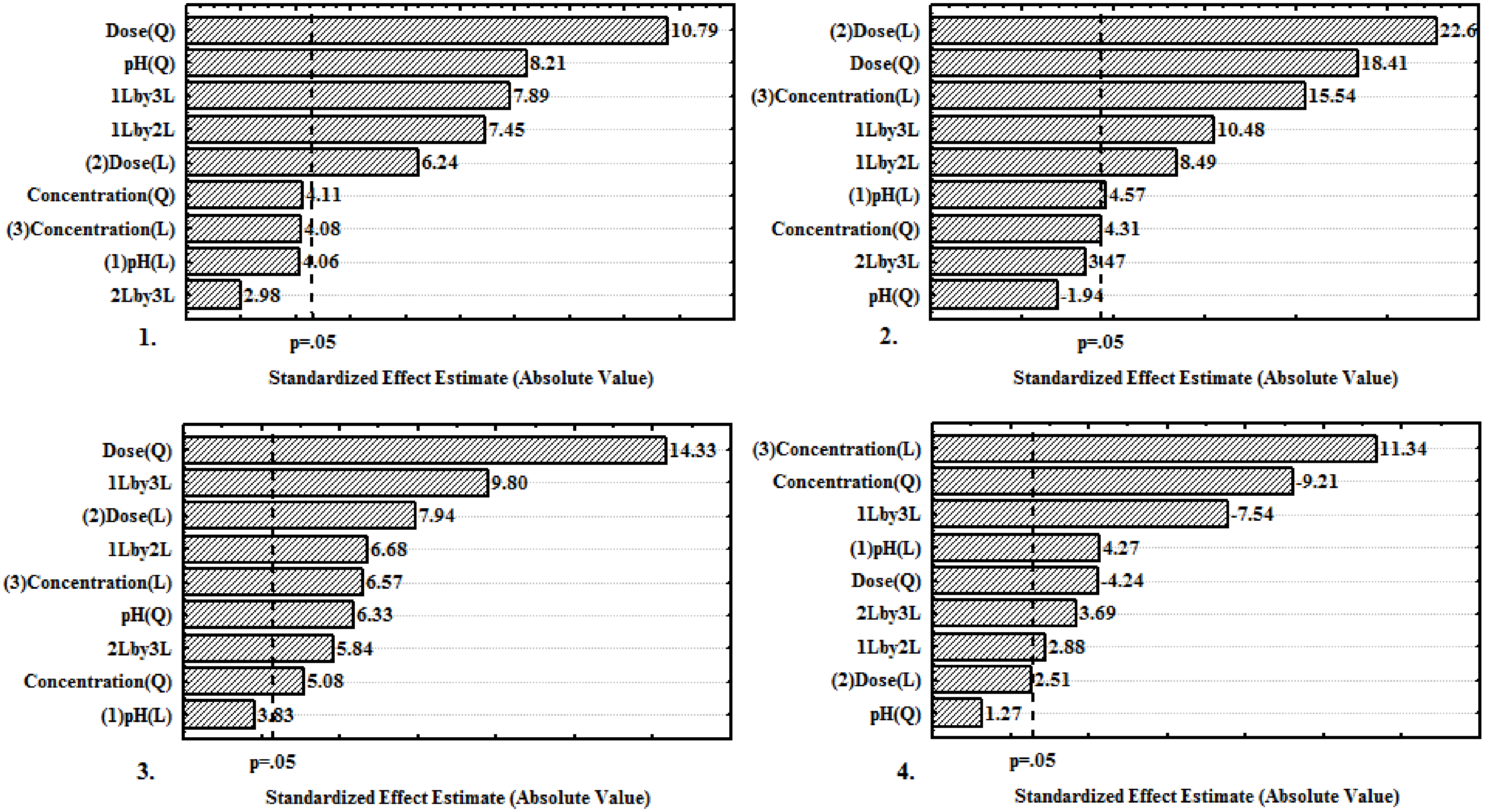


Figure 5.14. Standardized Pareto chart for main and interaction factors of 1.bromophos methyl, 2. quinalphos, 3. pretilachlor and 4. CR removal by UTL

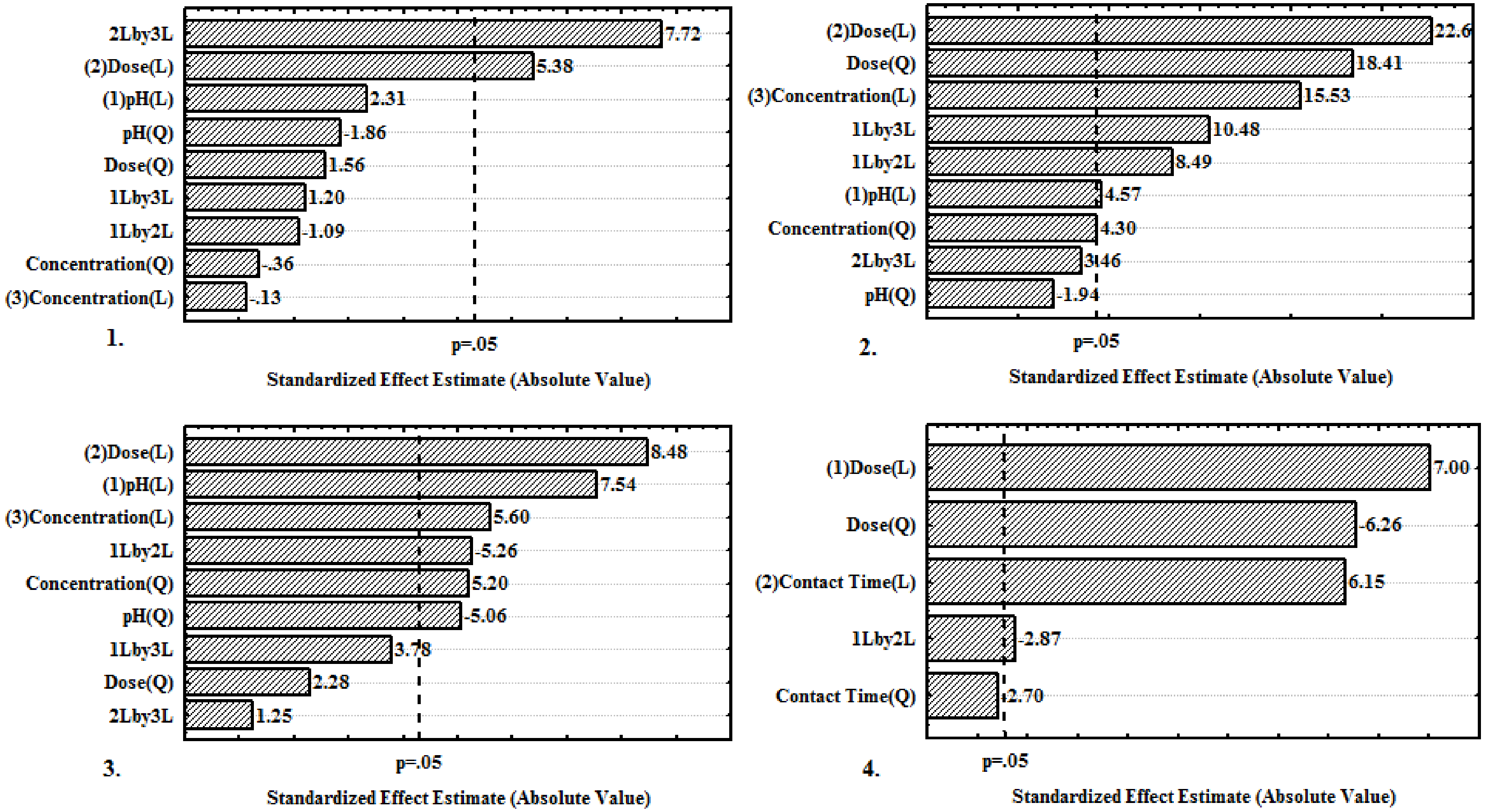


Figure 5.15. Standardized Pareto chart for main and interaction factors of 1.bromophos methyl, 2. quinalphos, 3. pretilachlor and 4. CR removal by SD

Table 5.14. Predicted model regression equations obtained for target compounds in terms of significant actual factors

NLP

Compounds	Regression equations
Bromophos methyl	Removal %= -48.75 + 936.23*Dose – 1038.41*Dose^2 – 53.30*pH*Dose
Quinalphos	Removal %= 57.24 + 596.92*Dose - 1325.65*Dose^2 – 9.79*Concentration + 0.60*pH*Concentration
Pretilachlor	Removal %= 64.05 + 1.19*pH^2 + 457.29*Dose – 1022.29*Dose^2 - 8.29*Concentration - 21.25*pH*Dose + 0.58*pH*concentration
Congo red	Removal %= + 9.67*pH + 212.02*Dose + 0.73*concentration - 11.26*pH*Dose - 0.06*pH*Concentration

UTL.

Compounds	Regression equations
Bromophos methyl	Removal %= – 1.86*pH + 491.50*Dose – 978.50*Dose^2 + 32.46*pH*Dose + 1.15*pH*Concentration
Quinalphos	Removal %= - 10.14*pH + 516.15*Dose - 770.75*Dose^2 - 3.24*Concentration – 0.20* Concentration^2 + 17.09*pH*Dose + 0.70*pH*Concentration
Pretilachlor	Removal %= – 1.16*pH^2 + 584.00*Dose -1046.83*Dose^2 - 7.74*Concentration - 0.41*Concentration^2 - 23.46*pH*Dose + 1.15*pH*Concentration + 13.66*Dose*Concentration
Congo red	Removal %= 38.11 – 212.90*Dose^2 + 1.28*Concentration - 0.01*Concentration^2 + 9.71*pH*Dose – 0.10*pH*Concentration + 0.99*Dose*Concentration

SD

Compound	Regression equations
Bromophos methyl	Removal %= – 10.89*Concentration +29.49*Dose*Concentration
Quinalphos	Removal %= - 6.94*pH + 353.5*Dose - 527.19*Dose^2 - 2.22*Concentration – 0.14* Concentration^2 + 11.69*pH*Dose + 0.48*pH*Concentration
Pretilachlor	Removal %= + 1.19*pH^2 + 396.79*Dose - 0.54*Concentration^2 - 23.70*pH*Dose
Congo red	Removal %= -113.14 + 208.65*Dose – 69.18* Dose^2 + 33.05*Contact time – 10.45*Dose * Contact time

5.4.7. *Models and effects of different factors on removal of selected compounds*

The final predicted mathematical model in terms of significant actual factors for bromophos methyl, quinalphos, pretilachlor and congo red removal% by different low cost materials is presented in **Table 5.14.**

5.4.7.1. Removal by neem leaves powder (NLP)

For bromophos methyl (**Table 5.14)** it has been seen that the main effect of adsorbent dose have positive significant effect on removal percentage. If adsorbent dose increases, the removal percentage of bromophos methyl also increases. The interaction effect of pH and dose have negative significant on removal. From **Figure 5.16a,** it has been seen that if dose and pH simultaneously increases then removal% decreases and with low pH and high dose resulted the highest removal percentage of bromophos methyl. This observation indicates, at certain point, surface of the NLP is fully covered by the bromophos molecules and don't have capability to adsorb more molecules resulting lower removal percent. From the zeta potential measurement of NLP at different pH, it has been seen that at pH 4.5, surface charge tends to more negative and after pH 4.5; negative surface of NLP is not suitable for anionic molecules and produce lower adsorption.

The main effects of adsorbent dose have positive significant impact on quinalphos removal percentage due available active site, on the other hand, negative significant of concentration also observed **(Table 5.14)**, it can also be expressed that if the initial concentration increases the removal percentage of quinalphos decrease. Suggesting limiting number of sorption sites available for sorption at higher concentration. The interaction effect of pH and concentration **(Figure 5.16b)** indicates that increase of pH and concentration resulted more removal percentage. A higher initial concentration provides an important driving force to overcome all mass transfer resistances of the quinalphos between the aqueous and solid phases, thus increases the uptake (Aksu and Tezer, 2005). This result may be explained by the fact that, at very low pH values, the surface of adsorbent would also be surrounded by the hydronium ions which enhance the quinalphos interaction with binding sites of the NLP by greater attractive forces. But as the pH increased, the overall surface charge on the adsorbent became negative and adsorption decreased.

The significant main effects factors for pretilachlor removal percentage were adsorbent dose and concentration, whereas quadratic effect of pH and dose also was significant. The interaction effect of pH vs dose and pH vs concentration has been represented in **Figures 5.16c&d**. The negative interaction effect of dose and ph expressed that if pH increases and dose decreases then removal percentage also decreases. This observation may be attributed the low adsorbent dose capacity of the surface due to the low quantity of adsorbents active sites for the attraction of pretilachlor molecules.

All the main effect of selected factors had significant positive impact on removal of congo red. But on the other hand, both of the significant interaction effect was negative, indicating, separately there has no role any factors for removal. Form **Figure, 5.16e** it can be illustrated that if pH and dose increased simultaneously then removal% increased at certain point but after pH 6, removal percent also decreased gradually with dose. This fact reveled that the increases of adsorbent dose, increases removal percentage until the activity of the surface functional groups. From FTIR analysis, it has been proved that NLP powder possess lots of oxygen containing functional groups (carboxylic acids, phenol, alcohol, ketone etc.). At high pH, NLP surface is occupied by these anionic functional groups and did not permit the same anionic charged dye due to inter ionic repulsion between similar charged particle., as we know that congo red is a dipolar molecular, it exists anionic form at basic pH. Thus, the extent of dye adsorption on the surface of NLP is low at high pH. At acidic pH, the dye molecule exists as cations and at this pH, active site of NLP contains all active functional groups. Cationic dye molecules get attached on the surface of NLP by replacing H^+ ion of carboxylic and phenolic ion. Therefore, adsorption of congo red on the NLP surface is much higher at acidic pH. In **Figure 5.16f**, describe the interaction effect of pH and concentration on removal of CR and it explained that the simultaneous increases of pH and concentration will give reduced removal percentage. The highest removal% is obtained with pH and concentration in ranges of low pH and high concentrations; nevertheless, the pH effect becomes less important when the concentration level increases.

5.4.7.2. Removal by Uesd tea leaves (UTL)

The main effect of pH and dose had significant role for the removal of bromophos methyl on UTL as it is observed from the **Table 5.14**. **Figures 5.17a&b** represented the 3D response surface plots of pH vs. dose and pH vs concentration.

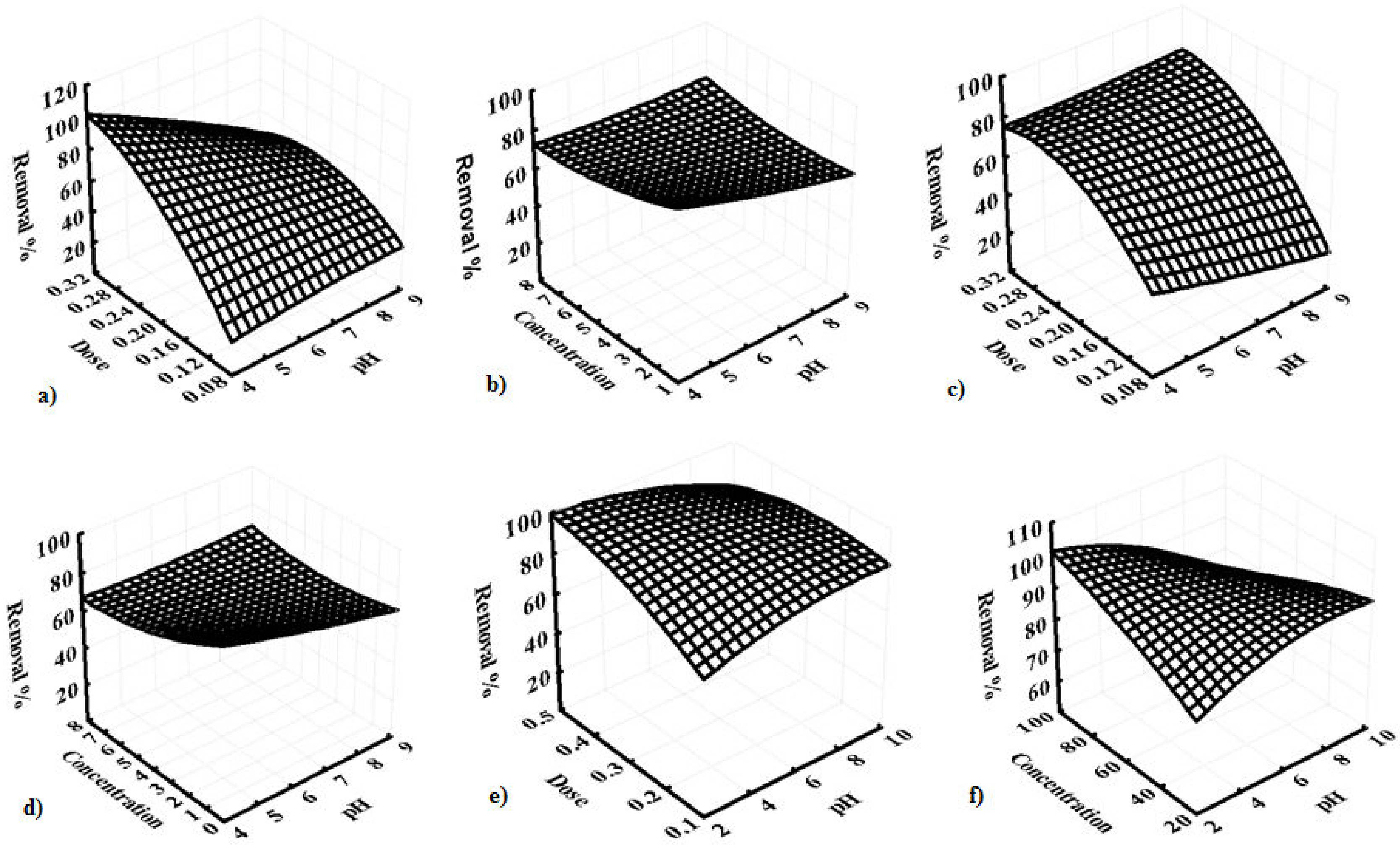


Figure 5.16. 3D response surface plots for (a) bromophs methyl, (b) quinalphos, (c&d) pretilachlor and (e&f) congo red onto NLP

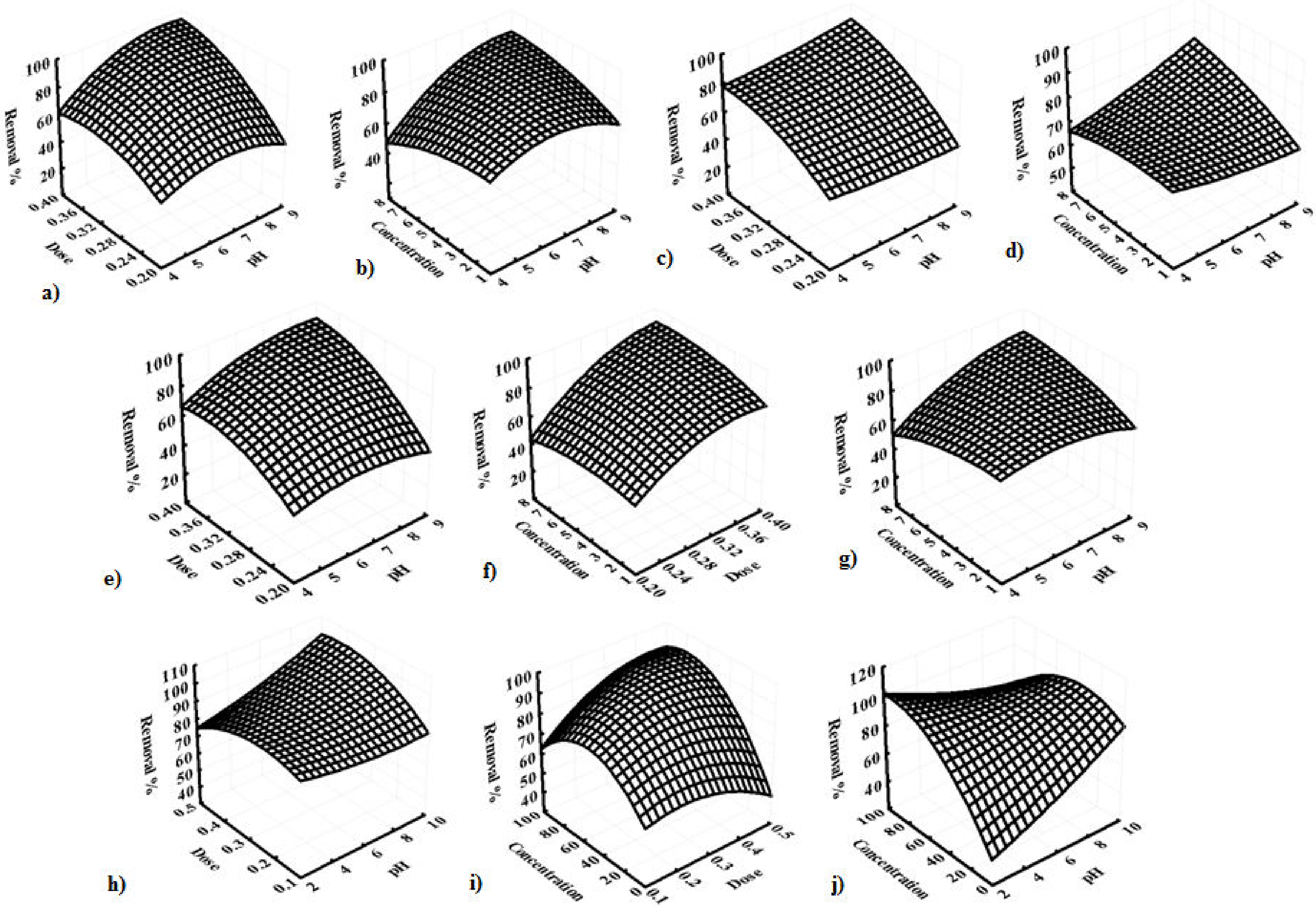


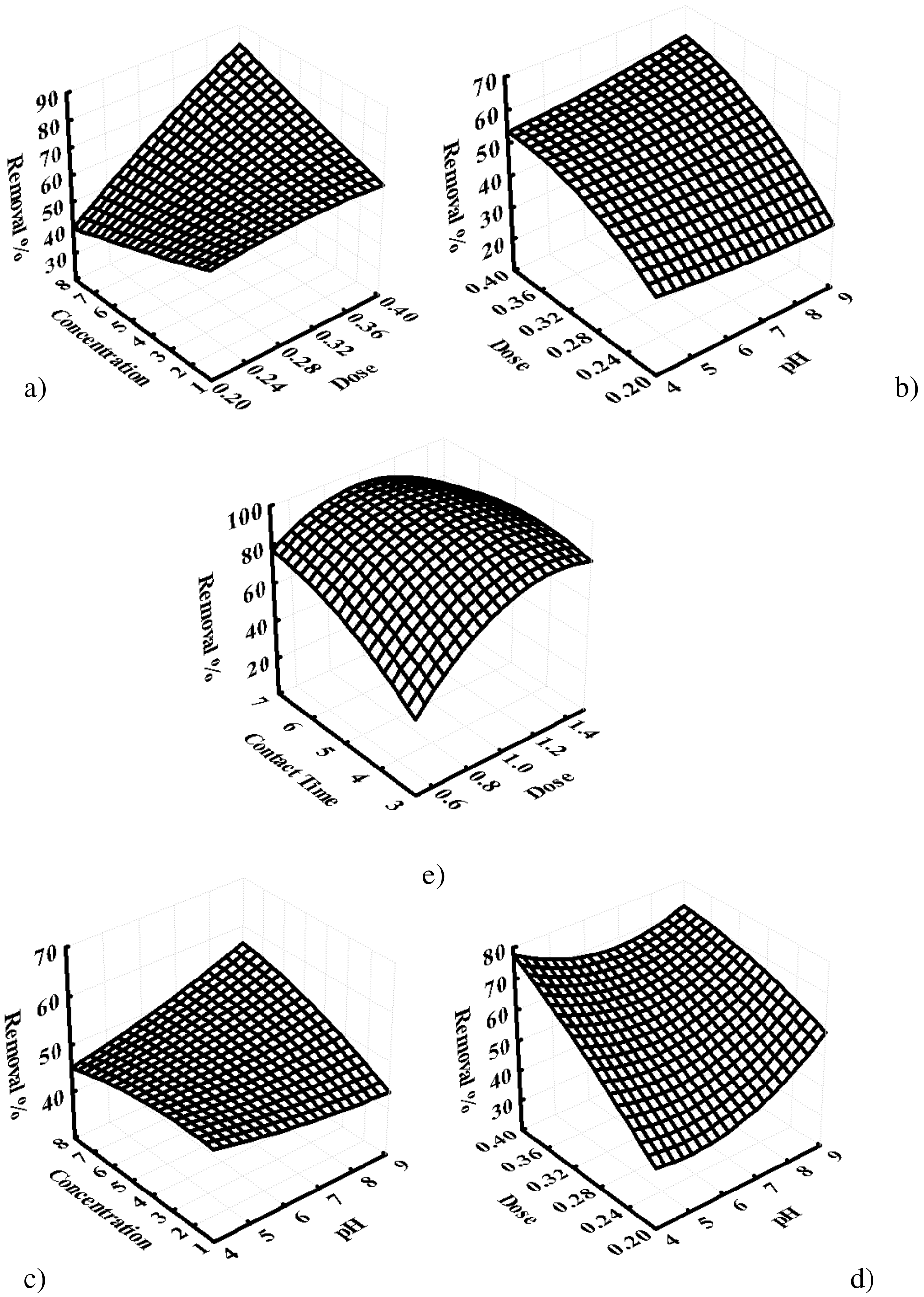
Figure 5.17. 3D response surface plots for (a & b) bromophs methyl, (c&d) quinalphos, (e,f&g) pretilachlor and (h,i&j) congo red onto UTL

From **Table 5.14**, it has been observed that the main effects of pH and concentration had significant negative effect on removal; if pH or concentration increased then removal percent may be decreased. The surface charge (zeta potential) of the bio-adsorbents plays a vital role in electrostatic adsorption on the biomaterial. The zeta potentials of the used tea leaves (data not shown) under different pH were negatively charged, indicating the affinity of used tea leaves for cations. The maximum negative charge of the used tea leaves was found at pH 6 and afterwards its values are slightly positive. Therefore, at high pH value, negatively charged surface of used tea leaves dissociate the anions and resulted into lower removal percent. On the other hand, although, quinalphos is nonionic compound, without strong acidic or basic functionalities. But an increase of concentration in the solutions decreases the removal percentage of quinalphos. At low concentration, surface activity of used tea leaves is higher and resulted more removal% but at high concentration, the active sites of adsorbent gradually covered by the molecules and showed lower removal percent. From **Table 5.14**, it has been also observed that the main effect of adsorbent dose had the highest positive significant impact on removal of quinalphos from aqueous solution, indicating increases of adsorbent dose increases the removal percent due to more available active surface site. The interactions effect of pH and adsorbent dose had positive significant impact on removal% of quinalphos as it is observed from the model and this interaction is depicted in **Figure 5.17c**. For instance, at constant initial concentration (4 mg L^{-1}), for pH 5 and adsorbent dose 0.2 g gave 47.12% of removal but increasing dose at 0.4g with the same pH 5, produced 81.17% of removal. Afterwards, when pH increases (pH 9) and dose decreases at 0.3 g, the removal% also decresed. Finally, at pH 7 with 0.2g adsorbent dose resulted the lowest removal% (41%). From above observations, it can be established that for interactions of pH and adsorbent dose, adsorbent dose mainly governed the removal% of quinalphos and there has no marked influence of pH for this. Quinalphos has phosphorus atom (P) in its aromatic ring and P has affinity to nitro, cyano, halogen, ketone, and carboxylic ester that are the active functional group on adsorbent obtained from FTIR analysis. The increses of adsorbent dose, increses the amount of surface area of adsorbents as well as the activity of functional groups and finally produced higher removal%. On the other hand, when dose kept constant (0.3g), the interaction effect of pH and concentration showed the same influence of pH **(Fig.5.17d)**. For example, at pH 5 and concentration 7 mg L^{-1} , 69% of removal was obtained and further increment of pH 9 with the same concentration guided more removal% (80.81%). The highest removal%

(86.67%) was obtained at the combination of medium pH and high concentration. It was also noticed that at pH 7 and concentration 1 mg L^{-1} , reduced removal% (74.09%) observed. Therefore, for the interaction effect of pH and initial concentration, the latter was mostly responsible for removal efficiency and the pH effect becomes less important when the concentration level increases.

From **Table 5.14**, it has been observed the adsorbent dose play a vital role for the removal of pretilachlor whereas pH and concentration had negative significant impact on removal percentage. All the interaction effects **(Figures 5.17e, f&g)** were significant suggesting that the roles of all factors on way of adsorption.

It may be said that the linear effect of pH and adsorbent dose had not significant effect on removal of CR dye by UTL. But on the other hand, the main effect of initial dye concentration showed a positive significant impact on removal percent. It is evident that initial concentration increases, the removal percentage of dye increases. According to the Aksu and Tezer (2005), a higher initial concentration gives an important driving force to overwhelm all mass transfer resistances of the dye between the aqueous and solid phases, hence increases the removal percent. Then again, the quadratic effect of adsorbent dose and concentration were significant effect on removal% of CR red. Interactions effect of all factors have significant role for removal of CR onto used tea leaves. The synergistic effect between adsorbent dose and pH in **Figure 5.17h** was significant for CR removal onto used tea leaves and indicating, at high pH with high adsorbent dose gave the highest removal% of CR dye. It may be attributed by this fact that the adsorbent can be used in wider range of pH if higher adsorbent dose is use. **Figure 5.17i** represents the interaction effect of adsorbent dose and concentration. The removal% of CR increases with increasing concentration and adsorbent dose but removal% was decreased after certain point of adsorbent dose, indicating that vacant sites of used tea leaves were filled by the CR molecules with increasing concentration. In **Figure 5.17j**, it can be stated that the interaction effect of pH and concentration has negative effect on removal of CR, indicates simultaneous increases of pH and concentration will give reduced removal percentage. The highest removal% is obtained with pH and concentration in ranges of low pH and high concentrations; nevertheless, the pH effect becomes less important when the concentration level increases.



a) b) e) c) d)

Figure 5.18. 3D response surface plots for (a) bromophs methyl, (b&c) quinalphos, (d) pretilachlor and (e) congo red onto SD

5.4.7.3. Removal by sawdust (SD)

Concentration had negative significant role for the removal of bromophos methyl by sawdust as it is observed from the **Table 5.14** indicating increases of concentration decreases the removal of bromophos methyl. This observation suggested that the limiting number of sorption sites available for sorption at higher concentration of sorbate molecules. This effect may also be interpreted that at low sorbate ion/sorbent ratios, sorbate ion sorption involves the higher energy sites. As the sorbate ion/sorbent ratio increases, the higher energy sites are saturated and sorption begins on lower energy sites, resulting in a decrease in removal efficiency (Sivaraj et al., 2001). But the interaction effect of dose and concentration showed positive impact on removal. From **Figure 5.18a**, it has been observed that at the highest dose and the lowest concentration causes the highest removal percentage by the sawdust. The cell walls of sawdust mainly consist of cellulose and lignin, and many hydroxyl groups, such as tannins or other phenolic compounds. All those components are active ion exchange compounds. Lignin, the third major component of the wood cell wall, is a polymer material. Lignin molecule is built up from the phenylpropane nucleus, i.e. an aromatic ring with a three carbon side chain. Vanillin and syringaldehyde are the two of other basic structural units of lignin molecule. When adsorbent dose increased, the quantity of surface area also increased, thus the activities of active ion exchange compounds present on surface enhanced that provoked the higher removal percentage

For the removal of quinalphos by sawdust, the linear effect of dose had positive impact on removal but pH and concentration had negative impact. The quadratic effect of dose and concentration had also significant role on removal of quinalphos by SD. **Figure 5.18b** indicating, at high pH with high adsorbent dose gave the highest removal% of quinalphos attributed by this fact that the adsorbent can be used in wider range of pH if higher adsorbent dose is use. The interaction effect of pH vs. concentration had significant positive effect on quinalphos removal onto SD. As pH and concentration increases, anionic molecules of pesticide in solution increased and difficult for adsorbing by the adsorbent finally decrease the removal% **(Figure 5.18c)**.

For pretilachlor removal onto sawdust, the linear effect of adsorbent dose had highest impact on removal. But the interaction effect of pH and dose had negative significant effect. The removal was the highest at low pH and high adsorbent dose **(Figure 5.18d)**. The lowest concentration and medium pH values gave the highest removal percentage. On the other hand, the interaction effect of dose and concentration showed negative effect on removal of bromophos methyl. As observed from **Figure 5.18b**, the removal% of bromophos increases with increasing concentration and adsorbent dose but removal% was decreased after certain point of adsorbent dose, indicating that vacant sites of used tea leaves were filled by the pesticide molecules with increasing concentration.

For congo red, the liner effect of dose and contact time play main role for the removal. With higher contact time, the external mass transfer coefficient increases resulting higher removal of the dye molecules. But interaction effect of these two factors had negative effect on removal. It may be seen that the percentage adsorption increases with an increase in the contact time **(Figure 5.18e)** and attains equilibrium after some time, later when dye molecules saturated on the surface increase of contact time do not influence on the removal.

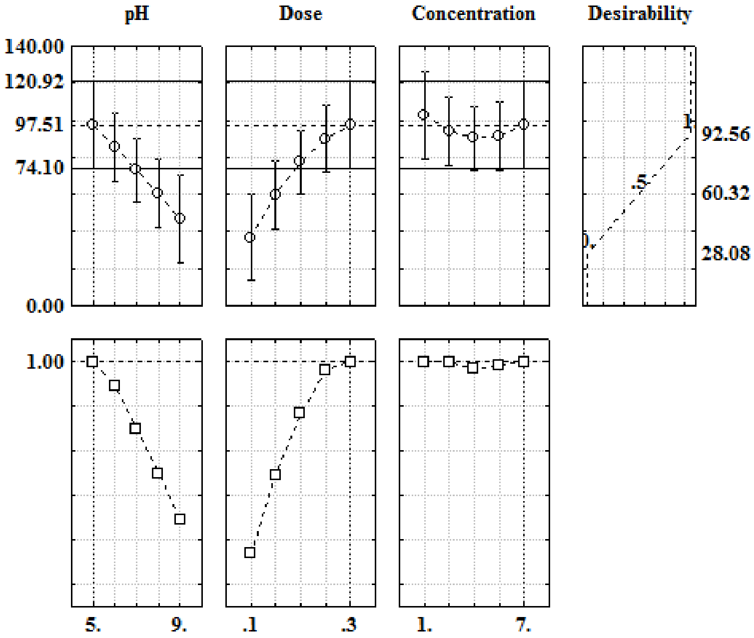


Figure 5.19. Profiles for predicated values and desirability function for bromophos methyl removal% by NLP. Dashed line indicated current values after optimization

5.4.8. *Optimization by using desirability function*

The optimization process was done by selecting software profile and desirability option. The detailed mathmatical appraoches of desirability function is described in section 2.7.1.5 of chapter two. The detailed procedures of building a optimization through desirability function also dicussed in section 4.4.8 of chapter four. In the similar way, optimization by desirability function was adopted in order to determine the optimum factors as well as response (removal %) for all compounds (including CR from CCD) onto different selected low cost materials **(Figure 5.19-5.30)**.

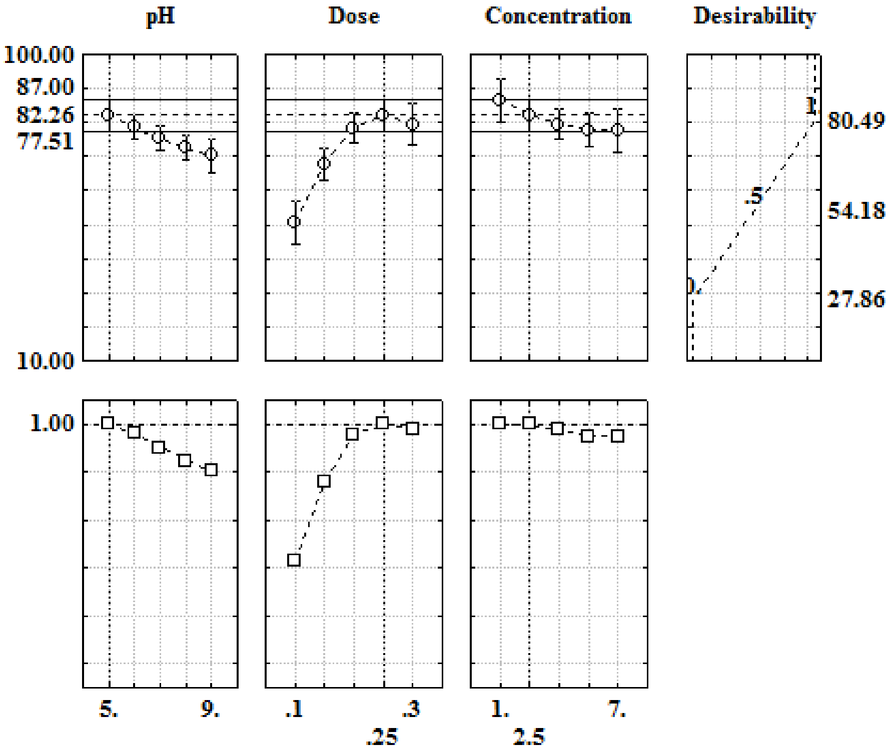


Figure 5.20. Profiles for predicated values and desirability function for quinalphos removal% by NLP. Dashed line indicated current values after optimization

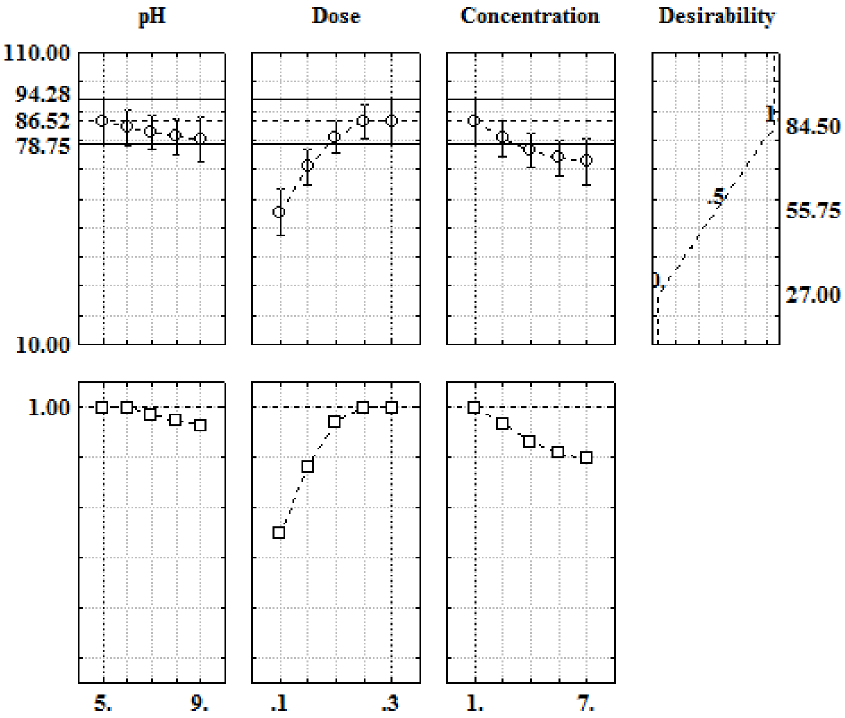


Figure 5.21. Profiles for predicated values and desirability function for pretilachlor removal% by NLP. Dashed line indicated current values after optimization

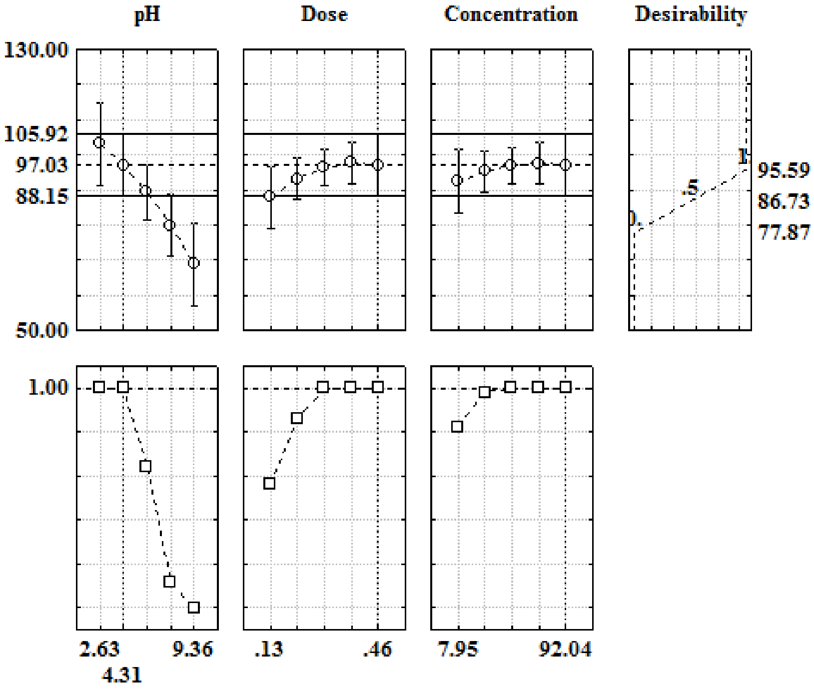


Figure 5.22. Profiles for predicated values and desirability function for congo red removal% by NLP. Dashed line indicated current values after optimization

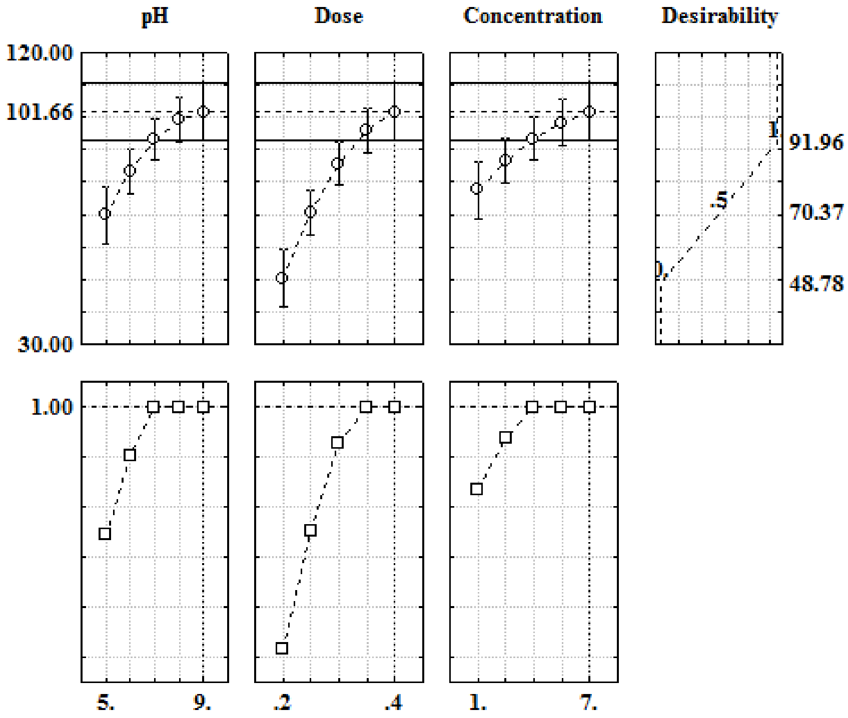


Figure 5.23. Profiles for predicated values and desirability function for bromophos methyl removal% by UTL. Dashed line indicated current values after optimization

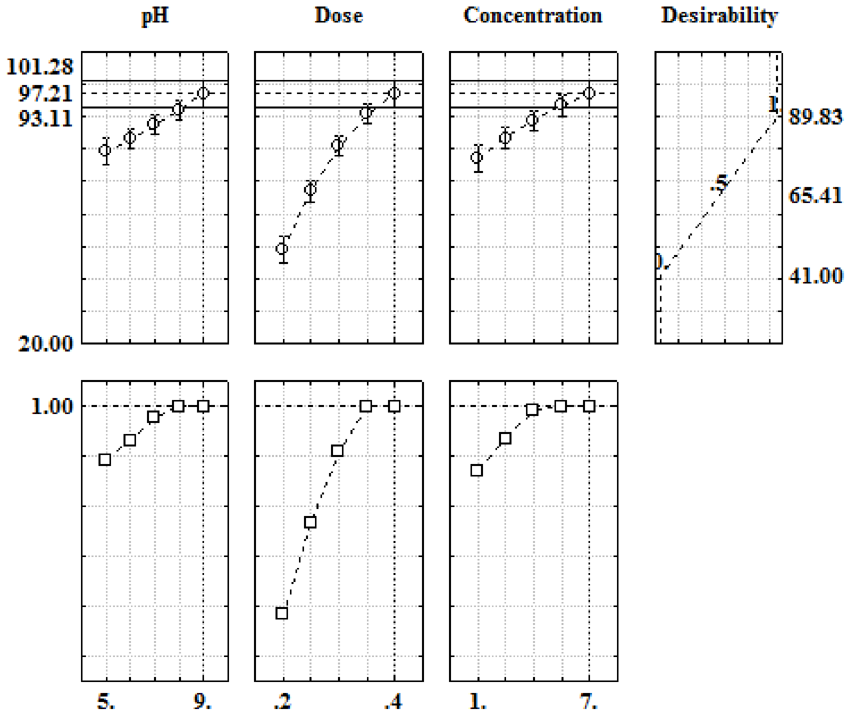


Figure 5.24. Profiles for predicated values and desirability function for quinalphos removal% by UTL. Dashed line indicated current values after optimization

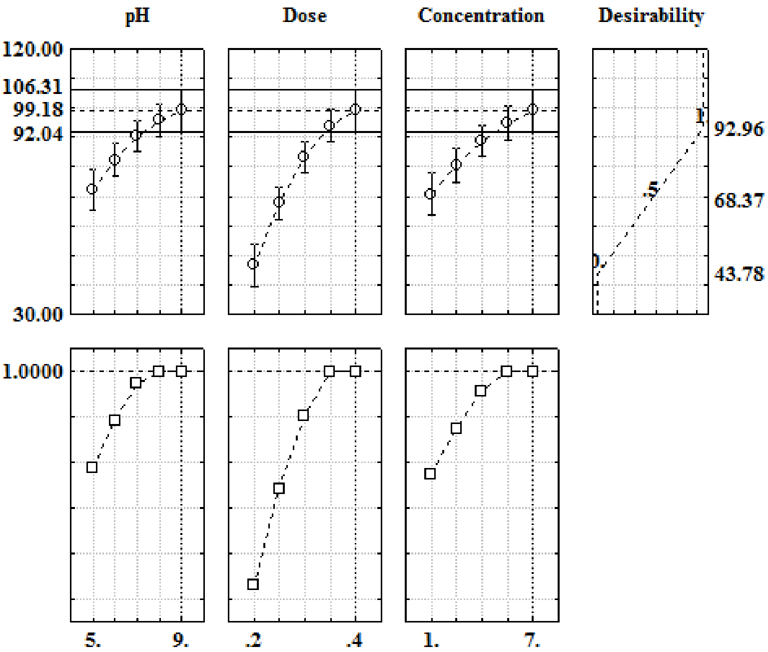


Figure 5.25. Profiles for predicated values and desirability function for pretilachlor removal% by UTL. Dashed line indicated current values after optimization

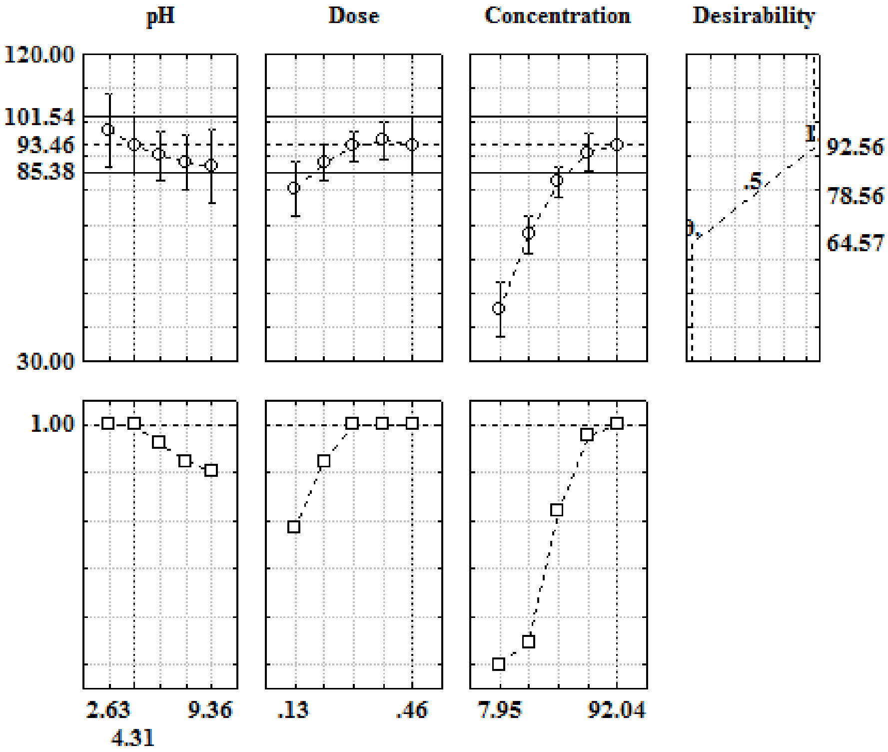


Figure 5.26. Profiles for predicated values and desirability function for congo red removal% by UTL. Dashed line indicated current values after optimization

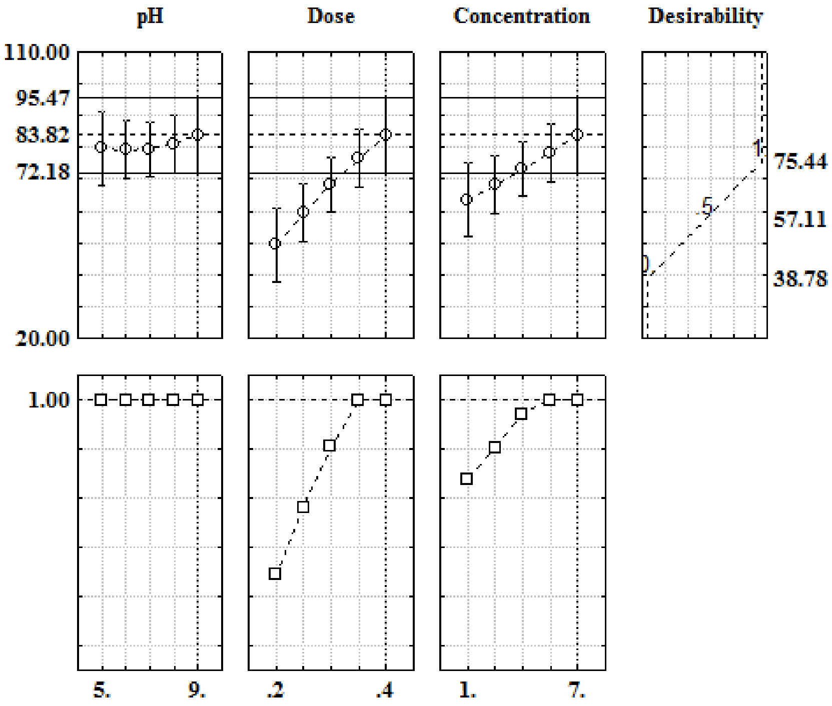


Figure 5.27. Profiles for predicated values and desirability function for bromophos methyl removal% by SD. Dashed line indicated current values after optimization

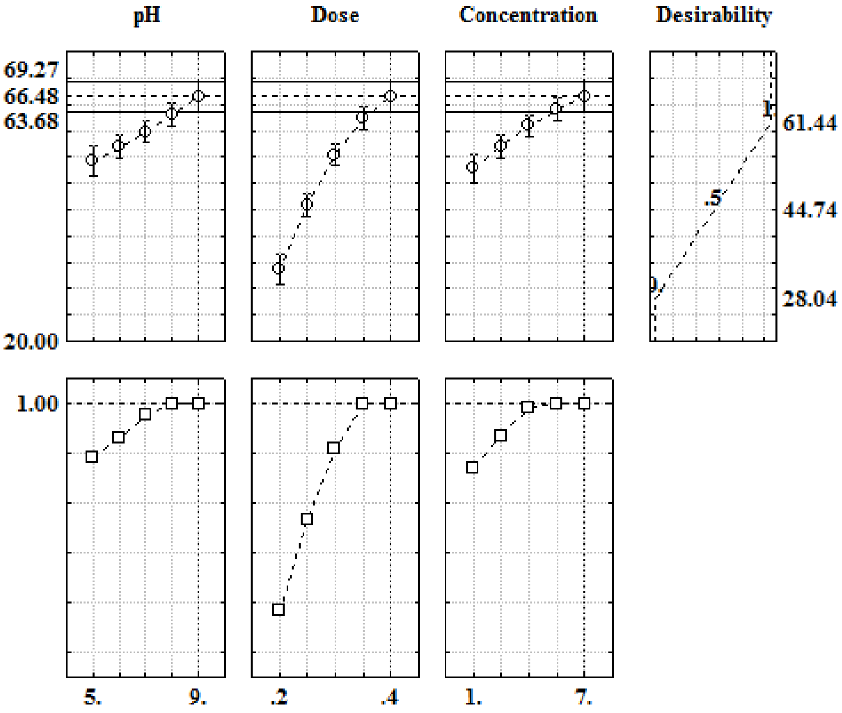


Figure 5.28. Profiles for predicated values and desirability function for quinalphos removal% by SD. Dashed line indicated current values after optimization

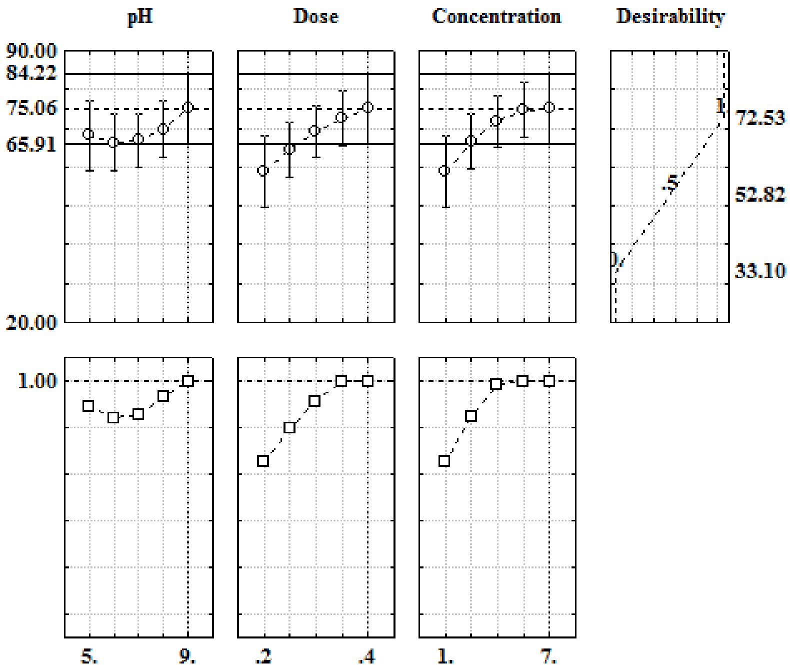


Figure 5.29. Profiles for predicated values and desirability function for pretilachlor removal% by SD. Dashed line indicated current values after optimization

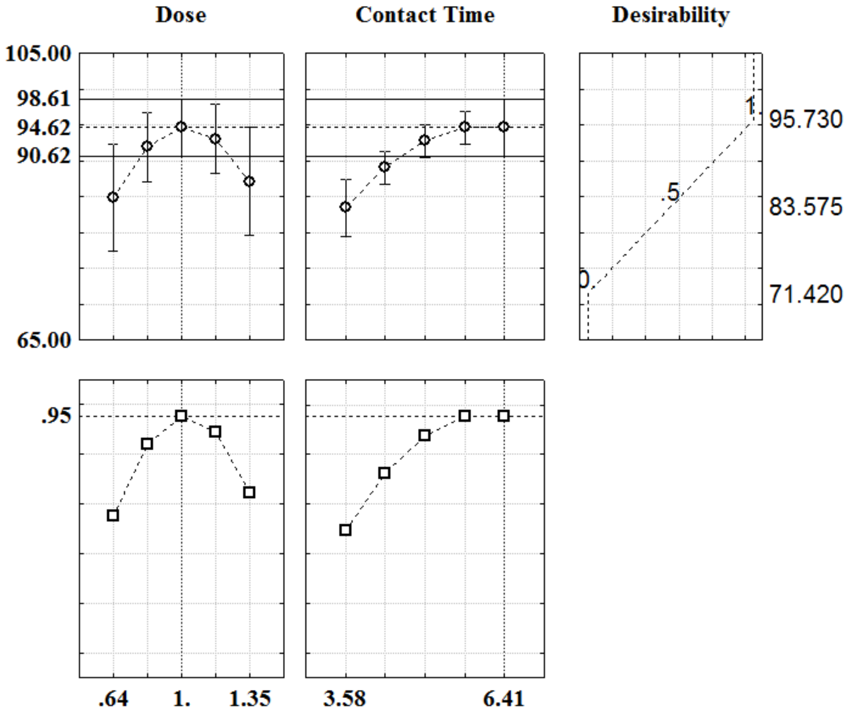


Figure 5.30. Profiles for predicated values and desirability function for congo red removal% by SD. Dashed line indicated current values after optimization

All the above aptimized factors value with their coresponding removal percentage for all compounds onto different adsorbents are also summarized in **Table 5.15**.

5.4.9. *Model validation*

Finally, validation as well as duplicate assenting experiments was performed using the optimized parameters obtained from multivariate RSM design for all compounds by selected adsorbents. The results are closely correlated with the data obtained from optimization analysis using Box-Behnken and CCD, indicating that RSM could be effiectively used to optimize the removal% for the studied adsorbents.

Table 5.15. Optmium values obtained from RSM based on desirability function and selected factors with their corresponding removal% for all pesticides and dye onto low cost adsorbents

Optimum value				
Bromophos methyl				
Materials	pH	Adsorbent dose(g)	Concentration (mg/L)	Removal %
NLP	5	0.30	7	97.51
UTL	9	0.40	7	101.66
SD	9	0.40	7	83.82
Quinalphos				
NLP	5	0.25	2.5	82.26
UTL	9	0.40	7.0	97.21
SD	9	0.40	7	66.48
Pretilachlor				
NLP	5	0.30	1	86.52
UTL	9	0.4	7	99.18
SD	9	0.40	7	75.06
Congo red				
NLP	4.31	0.46	92.04	97.03
UTL	4.31	0.46	92.04	93.46
		Adsorbent dose(g)	Contact time(hr)	Removal %
SD		1.00	6.41	94.62

5.4.10. *Adsorption isotherm*

In order to assess the potential adsorption capacity of the all low cost materials toward the pesticides and dye studied, adsorption isotherms at room temperature were derived on the basis of batch analysis with constant dose and pH obtained from the statistical optimization by desirability functions that has been presented in **Table 5.15**. Adsorption isotherm studies were carried out in 15 ml polypropylene centrifuge tubes with 10 ml of the different pesticides initial concentrations (0.5, 1.0, 2.5, 5.0 and 7 mg L^{-1}). For CR, 50 ml polypropylene centrifuge tubes with 25 ml of the different CR initial concentrations

(10, 25, 50, 75 and 100 mg L^{-1}) were examined. The extraction and analysis procedures were followed according to the previously discussed section 2.3 and 2.4.

All the adsorption isotherms were constructed for selected adsorbents using the linearized Freundlich and Langmuir isotherm equation according to equation discussed in previous chapter, section 4.4.10.

Langmuir and Freundlich isotherms parameters for the adsorption of all compounds onto different activated carbons are given in **Table 5.16**.

Table 5.16. Adsorption isotherm values of bromophos methyl, quinalphos, pretilachlor and congo red by Freundlich and Langmuir models

	Freundlich				Langmuir			
Com	Constants	NLP	UTL	SD	Constants	NLP	UTL	SD
Bromophos	K_F (mg g^{-1}(mg $l^{-1})^{-1/n}$)	1.30	1.00	0.60	q_m (mg g^{-1})	2.87	4.20	0.85
	1/n	1.21	1.20	1.33	K_a (l mg^{-1})	0.342	0.13	0.175
	R^2	0.936	0.943	0.845	R^2	0.964	0.928	0.828
	F_{error}	1.002	1.784	1.418	F_{error}	0.121	0.109	1.03
Quinalphos	K_F (mg g^{-1}(mg $l^{-1})^{-1/n}$)	0.40	0.40	0.30	q_m (mg g^{-1})	1.39	0.196	0.12
	1/n	0.93	0.98	0.93	K_a (l mg^{-1})	0.091	1.022	0.917
	R^2	0.951	0.956	0.967	R^2	0.962	0.963	0.917
	F_{error}	1.562	0.169	1.138	F_{error}	0.001	0.122	0.131
Pretilachlor	K_F (mg g^{-1}(mg $l^{-1})^{-1/n}$)	0.60	0.50	0.40	q_m (mg g^{-1})	9.09	14.28	0.49
	1/n	1.31	1.14	1.05	K_a (l mg^{-1})	0.017	0.009	0.279
	R^2	0.891	0.801	0.878	R^2	0.909	0.952	0.863
	F_{error}	1.001	0.281	1.265	F_{error}	0.153	0.001	0.108
Congo red	K_F (mg g^{-1}(mg $l^{-1})^{-1/n}$)	0.96	0.903	0.212	q_m (mg g^{-1})	78.74	6.41	2.94
	1/n	0.91	0.55	1.08	K_a (l mg^{-1})	0.011	0.087	0.011
	R^2	0.922	0.997	0.979	R^2	0.967	0.993	0.987
	F_{error}	0.135	0.057	0.261	F_{error}	0.013	0.001	0.031

The experimental isotherms data to Freundlich and Langmuir equations were also evaluated by error function in order to find out the best fit isotherm model.

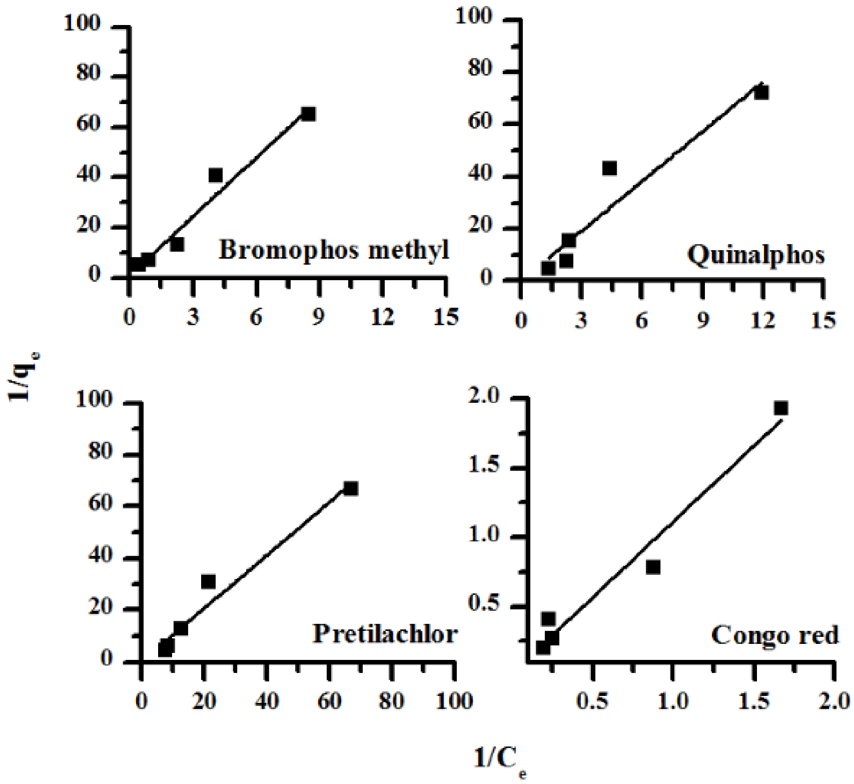


Figure 5.31. Langmuir isotherm plots of different compounds on NLP.

By comparing the results of the values of error function presented in **Table 5.16**, it can be concluded that the Langmuir model best fits the adsorption isotherm data for all adsorbents **(Figure 5.31, 5.32 and 5.33)**. Akhter and coauthors (2007) also observed the similar results for methyl parathion adsorption on different agricultural waste materials.

The monolayer adsorption capacity of Neem leaves powder (NLP) and used tea leaves (UTL) were found to be very good for all compounds in comparison to sawdust (SD). This observation attributed that the locally available as well as economically feasible adsorbents that have no alternative use showed high removal capacity for the removal of organic pollutants from the aqueous solution.

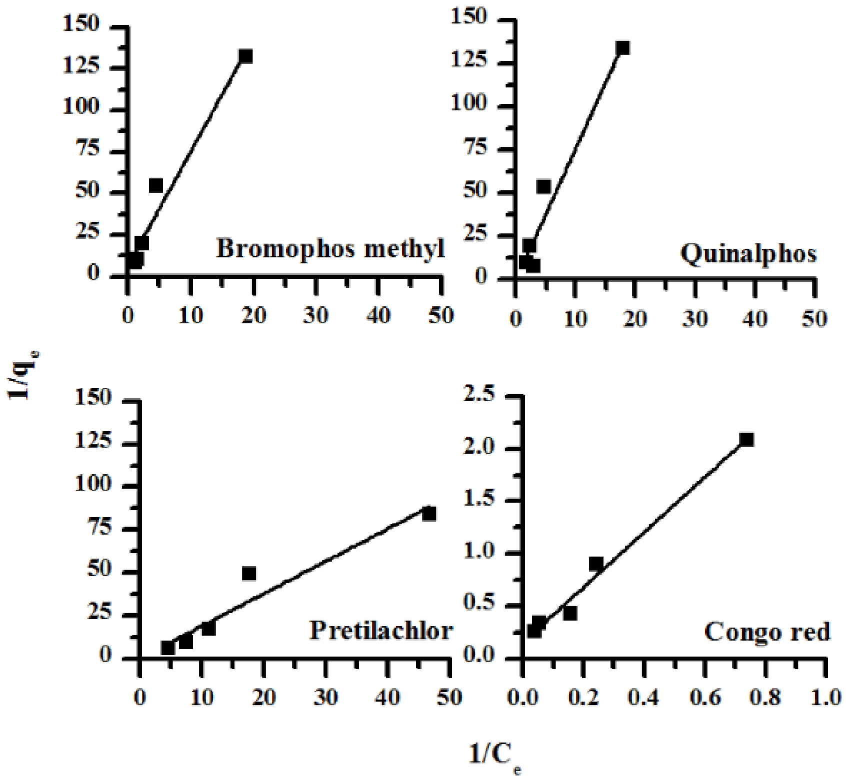


Figure 5.32. Langmuir isotherm plots of different compounds on UTL

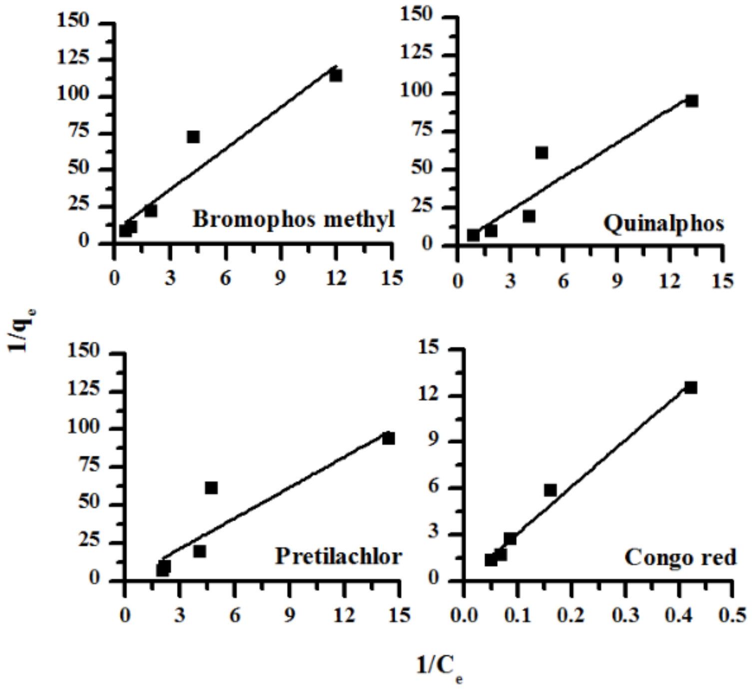


Figure 5.33. Langmuir isotherm plots of different compounds on SD

5.5. Conclusion

The Box-Behnken design and CCD was applied as a suitable response surface method to determine the effects of different adsorption parameters (pH, concentration and adsorbent dose) and their interactions, for removal of bromophos methyl, quinalphos, pretilachlor and congo red under optimal values of process parameters. The simultaneous optimization of the multi-response system by desirability function optimized very well. The adsorption isotherm was well fitted by the Langmuir model than Freundlich model, indicated homogenous surface structure. The adsorbents used in this study are locally available as well as economically feasible and there have no alternative use, moreover, proposed adsorbent do not require any pretreatments but showed high removal capacity. Although, single step of experiments did not remove 100% of selected compound from aqueous solution but 100% of removal may be possible by increasing dose or treatment of aqueous solution doubly. NLP and UTL can be use for the daily water treatments where these adsorbents are the most common and available and industrial treated water is beyond the capacity of common village people. Finally, it may be concluded that RSM with desirability function can provide a further insight for potential use of other processes, especially industrial waste water treatment system.

CHAPTER VI

A COMPARATIVE STUDY OF THE REMOVAL CAPACITY OF ACTIVATED CARBONS AND LOW COST MATERIALS USED IN THIS STUDY

Comparison of the removal capacity of different activated carbons (ACs) and low cost materials is presented in **Table 6.1**. Among the different studied ACs, for all pesticides and congo red, OSACs showed the highest removal capacity than other two ACs. Although the surface area of OSACs was higher, it is very difficult to draw a conclusion which factor(s) was responsible for the higher removal capacity of OSACs.

Table 6.1. Comparison between of activated carbons and low cost materials for the removal of pesticides and CR dye by this study

	Adsorption capacity q_m (mg g^{-1})					
Compounds	High cost materials ACs			Low cost materials		
	OSACs	RHACs	BAGACs	NLP	UTL	SD
Bromophos	11.11	5.26	1.23	2.87	4.20	0.85
Quinalphos	8.13	1.67	1.59	1.39	0.196	0.12
Pretilachlor	4.00	1.52	1.16	9.09	14.28	0.49
Congo red	33.90	6.08	3.27	78.74	6.41	2.94

On the other hand, among the different studied low cost materials, for bromophos methyl, UTL showed the highest removal capacity compared to NLP and SD. From **Table 6.1**, it may be also observed that the removal capacity of quinalphos by NLP is higher than UTL and SD while higher removal capacity of UTL was observed for pretilachlor removal (14.28 mg g^{-1}). But for congo red, the removal capacity of NLP was the highest (78.74 mg g^{-1}) among all low cost materials studied. The removal capacity by the SD was lower in all cases of analytes.

Table 6.2. Comparison of pesticides and CR dye removal by different activated carbons of this work and previous studies

Pesticides			
Adsorbents	Name of the pesticides	Removal capacity (mg/g)	References
Date stone activated carbon	2,4-D	238.10	Hameed et al. (2009)
Watermelon peels	Methyl parathion	6.39	Memon et al. (2008)
Activated carbon-cloth	Bentazon	151	Ayranci and Hoda (2004)
Activated carbon-cloth	Ametryn, aldicarb, dinoseb, diuron	354.61, 421.58, 301.84, 213.06	Ayranci and Hoda (2005)
Used tire AC	Paraquat	33.7	Hamadi et al. (2004)
Olive seed waste residue AC (OSACs)	Bromophos, quinalphos, pretilachlor	11.11, 8.13, 4.00	This study
Rice husk ACs (RHACs)	Bromophos, quinalphos, pretilachlor	5.26, 1.67, 1.52	This study
Bagasse ACs (BAGACs)	Bromophos, quinalphos, pretilachlor	1.23, 1.59, 1.16	This study

Congo red		
Adsorbents	Removal capacity (mg/g)	References
Commercial activated carbon	300.00	Purkait et al. (2007)
Different coal-based mesoporous activated carbons	52-189	Lorenc-Grabowska and Gryglewicz (2007)
ACs from plant material	21.17	Arivoli et al.(2008)
Olive stones activated carbon	167	Najar-Souissi et al.(2005)
Commercial grade and laboratory grade activated carbons	0.635 and 1.875 respectively	Mall et al.(2005)
OSACs	33.90	This study
RHACs	6.08	This study
BAGACs	3.27	This study

A comparative study of the removal capacity of different types of activated carbons used for the removal of pesticides and congo red is presented in **Table 6.2** and for low cost materials in **Table 6.3**.

Table 6.3. Comparison of pesticides and CR dye removal by low cost adsorbents of this work and previous studies

Pesticides

Adsorbents	Name of the pesticides	Removal capacity (mg/g)	References
Coal fly ash	Metolachlor	1.0	Sing (2009)
Sal wood charcoal	endosulfan	1.8	Mishra and Patel (2008)
Coal fly ash	metribuzin	0.56	Sing (2009)
Coal fly ash	atrazine	3.33	Sing (2009)
Neem leaves powder (NLP)	Bromophos, quinalphos, pretilachlor	2.87, 1.39, 9.09	This study
Used tea leaves, saw dusts (UTL)	Bromophos, quinalphos, pretilachlor	4.20, 0.196,14.28	This study
Saw dusts (SD)	Bromophos, quinalphos, pretilachlor	0.85, 0.12, 0.49	This study

Congo red

Adsorbents	Removal capacity (mg/g)	References
Banana peel	18.2	Annadurai et al. (2002)
Orange peel	14.0	Annadurai et al.(2002)
Neem leaf powder	41.2–28.3	Bhattacharyya and Sharma (2004)
Coir pith	6.72	Namasivayam and Kavitha (2002)
Jute stick powder	35.7	Panda et al.(2009)
lemon peel	34.5	Bhatnagar et al.(2009)
Neem leaves powder	78.74	This study
Used tea leaves	6.41	This study
Sawdust	2.94	This study

The physical and chemical properties of the adsorbent such as surface area, surface functional groups, surface charge and particle size determines the adsorption characteristics of a material. The surface properties of the low cost materials can be improved by various thermal and chemical treatments but it needs cost and sophisticated management. All the low cost materials used in this study are locally available as well as economically feasible and there have no alternative use, moreover, proposed adsorbents do not require any pretreatments but showed high removal capacity even than activated carbons. For instance, CR removal capacity by NLP was found to be highest among the all adsorbents studied. However, results show that UTL is a better adsorbent compared to some of the activated carbons. The comparative studies of the previous and present results revealed that the materials used in this study in some cases showed better capacity for the removal of hazardous compounds from the waste water.

CHAPTER VII

SUMMARY AND CONCLUSION

Adsorption desorption study was performed in order to evaluate the fate of three pesticides, bromophos methyl, quinalphos and pretilachlor, and a hazardous dye cong red on different Greek soils of various physicochemical properties. Desorption was carried out immediately after adsorption with water and afterwards with acetone. All the adsorption-desorption data were fitted to the Freundlich and Langmuir isotherm model and then a correlation study was performed between Freundlich adsorption coefficient (K_{fads}) with different soils parameters (organic matter content, pH and clay content) in order to determine the factor responsible for adsorption. Finally, the mean percent balance of adsorbed and desorbed amount of compounds by soils was calculated.

All the above mentioned pesticides and dye removal from aqueous solution were investigated using agro-based activated carbons namely, olive seed activated carbon (OSACs), rice husk activated carbon (RHACs) and bagasse activated carbon (BAGACs). The effect of pH, adsorbent dose and concentration on the removal of all compounds by activated carbons (ACs) was investigated using RSM based on Box Behnken and central composite design (CCD) in order to reduce the large number of experiments, time, cost and feasibility. For optimization of the process parameters and response, a multi-criteria decision approach "desirability function" was used. After optimization by desirability function, Langmuir and Freundlich adsorption isotherms were developed by using the optimized factors, in order to determine the potential removal capacity of studied activated carbons. Besides, kinetic study also performed in order to determine the rate of removal percentage by the selected activated carbons.

Sets of removal study were also carried out in order to determine the suitability of using low cost materials namely, neem leaves powder (NLP), used tea leaves (UTL) and sawdust (SD) for the removal of all selected compounds. Box Behnken and central composite design (CCD) was used as a statistical design of experiments for the evaluating of factors consider towards the removal. Like previous study, desirability function was also used for the optimization and afterwards isotherm studies were carried out in order to determine the removal capacity of the low cost materials. Finally, a comparative study was executed between the removal capacities of high cost activated carbon with low cost materials.

The following conclusions were drawn from this study:

i. Soil organic matter content is a major parameter that affects mainly the adsorption behavior of studied pesticides whereas clay content was responsible for dye adsorption.

ii. Adsorption and desorption studies expressed that the bromophos methyl, quinalphos, pretilachlor and congo red are not mobile to the environment. Soils with high organic matter content and clay content prevent these compounds to deteriorate the ground water.

iii. Bromophos methyl and congo red showed maximum adsorption and minimum desorption respectively. This suggests that these two compounds are relatively safe compounds than others concerning their bioavailability in the aqueous phase.

iv. RSM with desirability function was applied successfully in order to establish a relationship among the different removal processing factors (pH, adsorbent dose and concentration) with response (removal %) and suitable model were proposed for all compounds removal by activated carbons and low cost materials.

v. The experimental results showed that olive seed activated carbons, rice husk activated carbon and bagasse activated carbons can be used as effective adsorbent for the removal of bromophos methyl, quinalphos, pretilachlor and congo red dye from aqueous phase, the removal being dependent on pH, adsorbent dose and concentration of the compounds.

vi. Similarly, the Box-Behnken design and CCD was also applied as a suitable response surface method to determine the effects of different adsorption parameters (pH, concentration and adsorbent dose) and their interactions, for removal of bromophos methyl, quinalphos, pretilachlor and congo red under optimal values of process parameters onto neem leaves powder, used tea leaves and sawdust.

vii. The Langmuir isotherm model was the best-fitted with regard to isotherm than the Freundlich model for all cases.

viii. The pseudo-second order kinetics showed better results for adsorption process in the way of equilibrium for all compounds on all activated carbons and low cost materials.

ix. Olive seed waste residue activated carbon (OSACs) showed the best results in order to removal of all selected compounds from aqueous matrices than other ACs studied. On the other hand, neem leaves powder (NLP) and used tea leaves (UTL) showed better removal efficiency than sawdust and even better adsorbent compared to some activated carbons.

x. Therefore, low cost adsorbents used in this study for the removal of hazardous compounds from aqueous solution can be an effective alternative of high cost activated carbons for the daily water treatments where these adsorbents are the most common and available and industrial treated water is beyond the capacity of common village people.

RECOMMENDATIONS FOR FUTURE STUDIES

Determine the relative leaching potential of these compounds and determine transformation products of these compounds by soil micro-flora.

Further studies are needed for desorption studies, economically feasible regeneration of these adsorbents and application of these adsorbents for real industrial wastewater treatment by using response surface methodology.

CHAPTER VIII

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APPENDIX

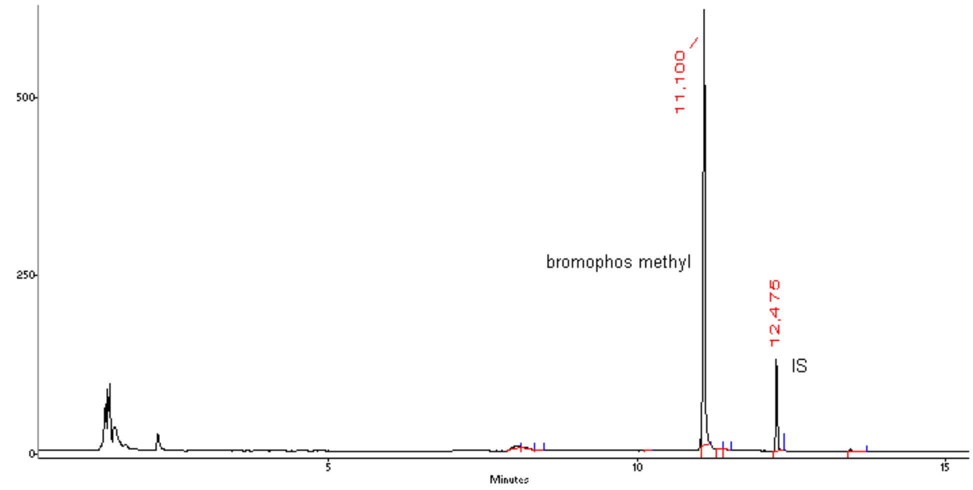

Figure 8.1. Chromatogram and retention time of bromophos methyl with internal standard (IS)

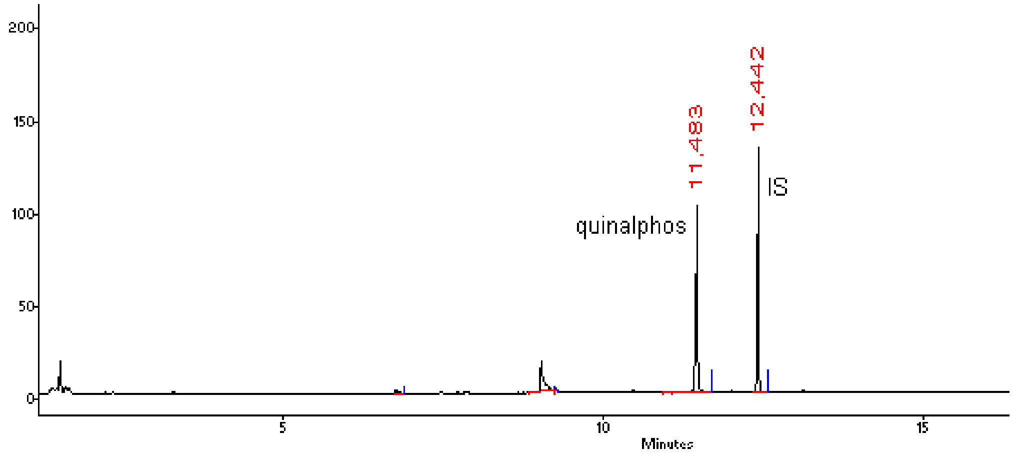

Figure 8.2. Chromatogram and retention time of quinalphos with internal standard (IS)

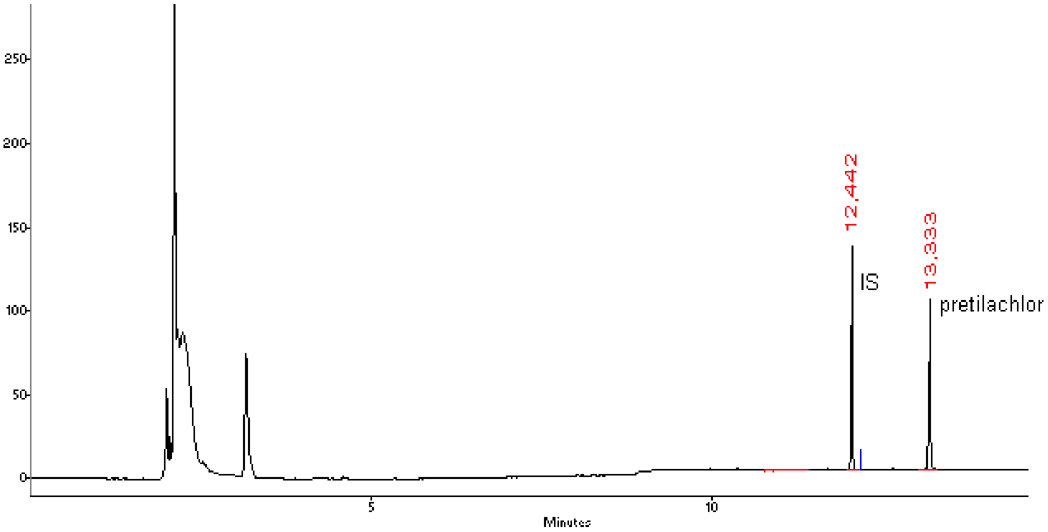

Figure 8.3. Chromatogram and retention time of pretilachlor with internal standard (IS)

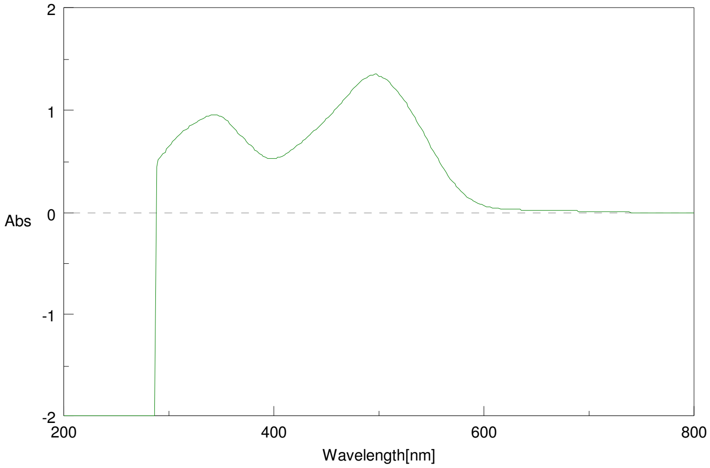

Figure 8.4. UV-spectra of congo red (CR) and λ_{max} at 496 nm

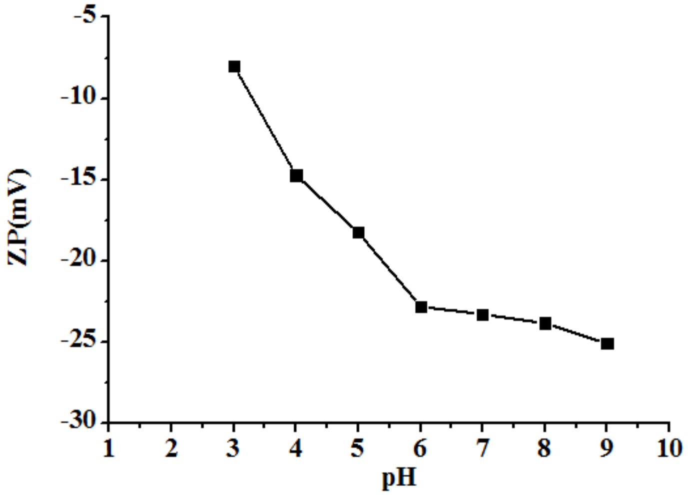

Figure 8.5. Zeta potential of OSACs

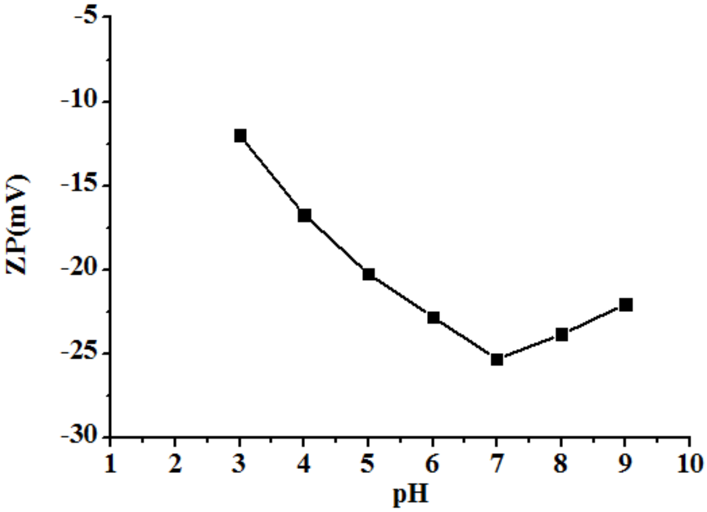

Figure 8.6. Zeta potential of RHACs

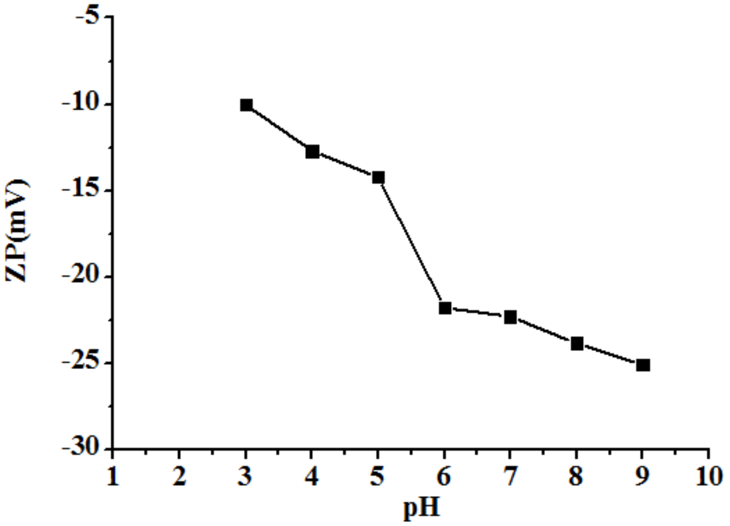

Figure 8.7. Zeta potential of BAGACs

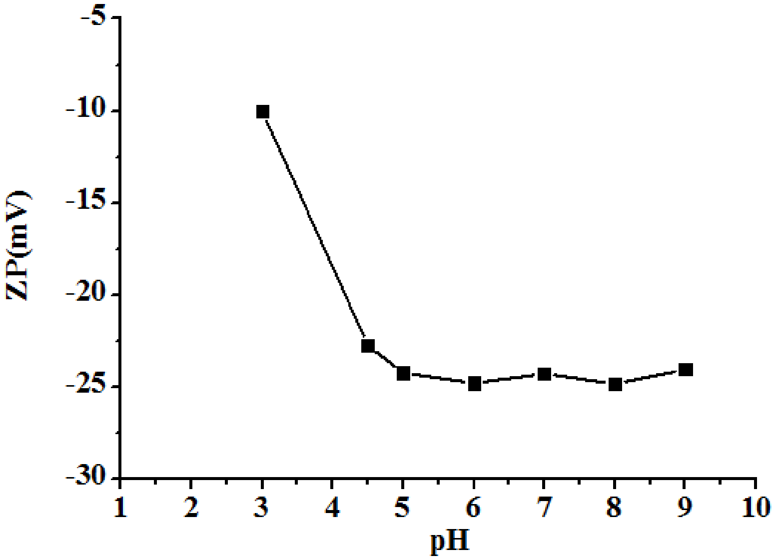

Figure 8.8. Zeta potential of NLP

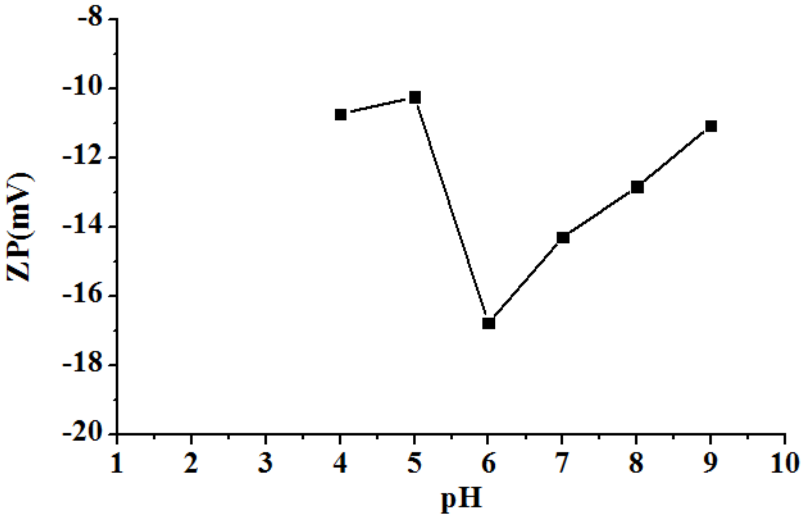

Figure 8.9. Zeta potential of UTL

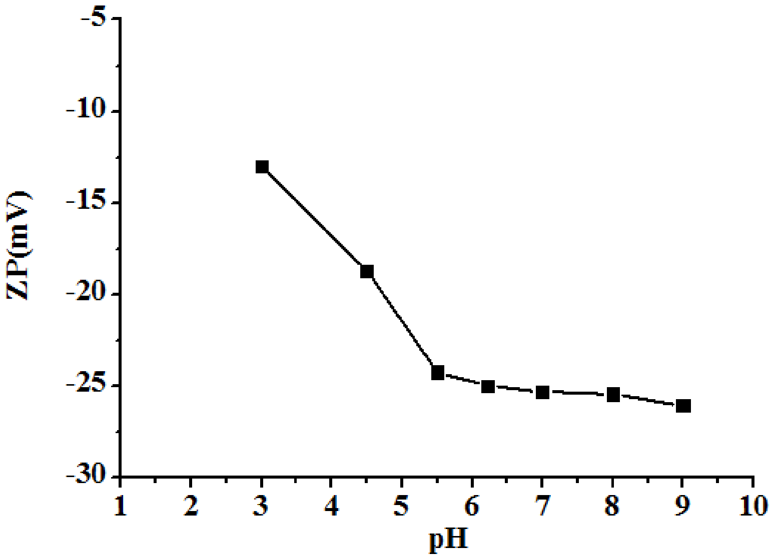

Figure 8.10. Zeta potential of SD

curriculum vitae

Personal information

Surname(s) / First name(s)	**Md. Azharul Islam**	
Address (es)	**Permanent Address** 43/44, West Barandipara Kadamtala Jessore- 7400. Bangladesh.	**Correspondence Address** Md. Azharul Islam X2-224, Lab of Environmental Chemistry Section of food and industrial chemistry Department of chemistry University of Ioannina 45110-Ioannina, Greece
Telephone(s)	+88 0421 61180 (Res. Bangladesh)	Tel. +30 26510-98363(Lab) Mobile: +30 6942 694457
E-mail(s)	iazharul@gmail.com iazharul@cc.uoi.gr	
Nationality(-ies)	Bangladeshi	
Date of birth	02/09/1976	
Father’s name	Ahmmad Ullah	
Mother’s name	Setara Begum	
Gender	Male	

Current status

Lecturer, Forestry and Wood Technology Discipline, Khulna University, Khulna 9208, Bangladesh.

Work experiences

Dates	October 2004 to August 2005
Occupation or position held	Lecturer
Main activities and responsibilities	Teaching and supervising the students
Name and address of employer	Forestry and Wood Technology Discipline, Khulna University, Khulna-9208, Bangladesh.
Type of business or sector	Public University
Dates	July- September 2004
Occupation or position held	Production Officer
Main activities and responsibilities	Monitoring as well as technical support and quality control of particle board production.
Name and address of employer	Akij Particle and Hardboard Mills Ltd., Tora Ghat, Ghior, Manikgong , Bangladesh.
Type of business or sector	Private Organization (A unit of Akij Group)

Education and training

Dates	2003
Title of qualification awarded	Masters of Science in Forestry (MS)
Principal subjects/Occupational skills covered	Thesis Title: 'Present status of using treated wood and private house owner’s expectations in Bangladesh '. Major subjects: Research Methodology, Wood Composite Products, Logging and Lumber Manufacturing, Wood Microbiology and Preservation, Wood Science and Engineering, Wood Properties and Utilization, Forest Management, Project Design and Management, Agroforestry,
Name and type of organisation providing organisation and training	Forestry and Wood Technology Discipline Khulna University, Khulna- 9208, Bangladesh.
Obtained CGPA/Marks	3.86 with Distinction in a scale of 4 Marks percentage: 72.07 %

Dates	2000
Title of qualification awarded	B.Sc. Honours in Forestry
Principal subjects/Occupational skills covered	Thesis Title: 'Study on some physical properties of sound and disease affected sissoo (*Dalbergia sissoo* Roxb.*)* wood'. Major Subjects: Geology & Soil Science; Forest Tree Physiology; Forest Ecology; Forest Genetics & Tree Improvement; Forest Entomology; Tea, Rubber & Non Timber Forest Product; Principle & Practice of Silviculture; Forest Mensuration; Mycology, Forest Pathology & Forest Protection; Mangrove Ecology; Aerial Photogrammetry & Remote Sensing; Silviculture of Species; Fuel Wood and Multipurpose Tree Species; Forestry Extension; Forest Harvesting; Coastal Afforestation; Soil Conservation and Watershed Management; Forest Inventory; Silvicultural Systems; Social Forestry and Rural Development; Mangrove Resources Management and Utilization; Agroforestry and Farming System; Forest Management, Wood Structure and Properties, Wood Physics and Mechanics, Wood Chemistry, Saw Milling, Saw Doctoring and Wood Working, Forest Harvesting and Transportation Engineering, Wood Seasoning and Preservation, Panel Products, Adhesion, Adhesives and Finishes, Pulp and Pulp Products etc.
Name and type of organisation providing organisation and training	Forestry and Wood Technology Discipline Khulna University, Khulna- 9208, Bangladesh.
Obtained CGPA/Marks	3.68 in a scale of 4 Marks percentage: 68.34 %

Dates	2002
Title of qualification awarded	Post Graduate Diploma in Information Technology (PGD IT)
Principal subjects/Occupational skills covered	Programming with visual tools, Networking and internet application, Programming in C/C^{++} , Operating system and UNIX, System analysis and software engineering, DBMS and database programming, Data structure and algorithm, Java programming, Client server technology, E-commerce, Business system, Project etc
Name and type of organisation providing organisation and training	Computer Science and Engineering Discipline Khulna University, Khulna- 9208, Bangladesh.
Obtained CGPA/Marks	2.77 in a scale of 4

Dates	2000
Title of qualification awarded	Diploma in Computer Science and Application
Principal subjects/Occupational skills covered	Desk-top Publishing, Microcomputer Trouble Shooting, Computer Networks, Office Automation, Computer Programming, Computer Basics, Database Management Systems, Microcomputers and Microprocessors, Digital Systems and Computer Organization, Operating System etc.
Name and type of organisation providing organisation and training	Bangladesh Open University, Gazipur 1705, Bangladesh.
Obtained CGPA/Marks	3.06 in a scale of 4

Personal skills and competences

Mother tongue(s) **BANGLA**

Other language(s)

Self-assessment	**Understanding**		**Speaking**		**Writing**
	Listening	Reading	Spoken interaction	Spoken production	
English	Proficient user	Proficient user	Proficient user	Proficient user	Proficient user

Social skills/ Organisational skills and competences	I have worked as an Election Observator of Bangladesh Parliament election 2001.
Computer skills and competences	I have completed Diploma and Postgraduate diploma in computer science.

Award Received

Prime Minister Award in 1993 for securing 9th position in combined merit list in Secondary School Certificate Examination.

Additional information

Publications

V.A. Sakkas, P. Calza, **M. Azharul Islam**, C. Medana, C. Baiocchi, K. Panagiotou and T. Albanis. 2009. TiO_2/H_2O_2 mediated photocatalytic transformation of UV filter 4-methylbenzylidene camphor (4-MBC) in aqueous phase: Statistical optimization and photoproduct analysis. *Applied Catalysis B: Environmental*. 90(3-4)526-534.

M. Azharul Islam, Vasilios Sakkas, Triantafyllos A. Albanis. 2009. Application of statistical design of experiment with desirability functions for the removal of organophosphorus pesticide from aqueous solution by low cost material, *Journal of Hazardous Materials*, 170(1)230-238.

M.N. Islam; A.A. Mahfuz; M.O. Hannan and **M.A. Islam**, 2006. Manufacture and properties of particle board from Dhaincha (*Sesbania aculeata*). *Journal of Biological Sciences*, 6(2); 417-419.

A.K.M.A. Bosunia; M.O. Hannan; A. A. Mahfuz; **M.A. Islam**; M.N. Islam; K. Mahmud and A.K. Lahiry, 2006. Study on Tanalith-E treatability of rubberwood (*Hevea brasiliensis*) grown in Bangladesh. *The International Research Group on Wood Preservation (IRG)*, Sweden. IRG/WP 06-40337.

A.A. Mahfuz; M.O. Hannan; **M.A. Islam**; M.N. Islam; M.M. Islam and A.K. Lahiry, 2006. Protection of a low-density mangrove timber species gewa (*Excoecaria agallocha*) through preparation of particleboard – An Assessment. *The International Research Group on Wood Preservation (IRG)*, Sweden. IRG/WP 06-40348.

A.K.M.A. Bosunia, **M.A. Islam;** M.M. Rahman and A.K. Lahiry. 2005. The present status, characters tics and problems of wood based timber handicrafts industry in Bangladesh. *The International Research Group on Wood Preservation (IRG)*, Sweden. IRG/WP 05-10545.

M.A. Islam; A.K.M.A. Bosunia; S.C. Ghosh; M.O. Hannan and A.K. Lahiry, 2004. Present status of using treated wood and private house owner's expectations in Bangladesh. *The International Research Group on Wood Preservation (IRG)*, Sweden. IRG/WP 04-30329.

S.C. Ghosh; A.K.M.A. Bosunia; **M.A. Islam** and A.K. lahiry**,** 2004. Physical properties variation of sound and top dying affected sundri (*heritiera fomes*) wood. *The International Research Group on Wood Preservation (IRG)*, Sweden. IRG/WP 04-10504.

M.A. Islam; M.S. Rahman; A.K.M.A. Bosunia and A.K. Lahiry, 2004. Present Status and potentiality of the economic utilization of the sawmill residue and wastage in Bangladesh. *The International Research Group on Wood Preservation (IRG)*, Sweden. IRG/WP 04-50211.

M.O. Hannan; S.M.M. Hasnin; M.S. Islam and **M.A. Islam**, 2001.Study on some physical properties of sound and disease affected sissoo (*Dalbergia sissoo* Roxb.*)* wood. *Khulna University Studies*, 3 (1):433-435.

Accepted article

M. Azharul Islam, Zacharoula Nikoloutsou, Vasilios Sakkas, Michalis Papatheodorou, Triantafyllos Albanis. Statistical optimization by combination of response surface methodology and desirability function for removal of azo dye from aqueous solution. In press, *International Journal of Environmental Analytical Chemistry*. GEAC-2008-0461.

M. Azharul Islam, Vasilios Sakkas, Triantafyllos A. Albanis. Adsorption-desorption study of bromophos methyl and quinalphos in Greek soils. In press, *International Journal of Environmental Analytical Chemistry*. GEAC-2008-0459.

Submitted article

M. Azharul Islam, Vasilios Sakkas, Triantafyllos A. Albanis. Removal of hazardous congo red dye from aqueous solution by olive seed activated carbon based on response surface methodology. *International Journal of Environmental Science and health, Part-A*. GEAC-2008-0460.

Vasilios Sakkas, **Md. Azharul Islam**, Constantine Stalikas, Triantafyllos Albanis, Photocatalytic degradation using Design of Experiments: a review and example of the Congo red degradation. *Journal of Hazardous Materials.*

Conference and seminar attended

Photolysis and photocatalysis 19-20 June, 2007, University of Ioannina, Greece

3rd Macedonian conference on chemistry in Thessaloniki, Greece, 14-17 March, 2008 (oral presentation).

AQUA 2008, 3rd International Conference: Water Science and Technology with emphasis on water & climate. 16-19 October 2008 - Athens, Greece (poster submission)

5th European Conference on Pesticides and Related Organic Micropollutants in the Environment and the 11th Symposium on Chemistry and Fate of Modern Pesticides. Marseille (France), October, 22nd-25th 2008 (poster submission).

Referees

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Declaration

My dated signature certifies that all information presented on these Curriculum Vitae is complete and correct to the best of my knowledge.

Signature:

Date: