Preparation of activated carbons from agricultural residues for pesticide adsorption

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ABSTRACT

Activated carbons (ACs) can be used not only for liquid but also for vapour phase applications, such as water treatment, deodorisation, gas purification and air treatment. In the present study, activated carbons produced from agricultural residues (olive kernel, corn cobs, rapeseed stalks and soya stalks) via physical steam activation were tested for the removal of Bromopropylate (BP) from water. For the characterization of the activated carbons ICP, SEM, FTIR and XRD analyses were performed. Adsorption kinetics and equilibrium isotherms were investigated for all biomass activated carbons in aqueous solutions. Experimental data of BP adsorption have fitted best to the pseudo 2nd-order kinetic model and Langmuir isotherm. The study resulted that corn cobs showed better adsorption capacity than the other biomass ACs. Comparison among ACs from biomass and commercial ones (F400 and Norit® GL50) revealed that the first can be equally effective for the removal of BP from water with the latter.

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1. Introduction

Leaching of chemical fertilizers and pesticides, applied to agricultural and forest land, is one of the main reasons for organic pollution in several water streams. Pesticides are greatly used in Europe. Particularly in Greece their use in crops is higher than the European average value. The pesticides are applied to the foliage of the crops, thus a considerable amount of the product results in soil. The removal of the pesticides by conventional biological treatments has proven to be ineffective, while activated carbons could be more effective. Thus, activated carbons are applicable to a wide range of processes for the removal of organic compounds in water (Li et al., 2002; Moreno-Castilla, 2004; Gupta et al., 2006; Dias et al., 2007).

ACs are adsorbents that are extremely porous and thus have a very large surface area available for adsorption or chemical reactions. Adsorption, like ion exchange and chromatography, is a sorption process in which certain adsorbents are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. Carbon adsorption has numerous applications in removing pollutants from air or water streams both in the field and in industrial processes such as spill cleanup, groundwater remediation, drinking water filtration, air

purification, volatile organic compounds removal, gasoline dispensing operations, and other processes. The adsorption process is generally classified as physisorption (characterized by weak van der Waals forces) or chemisorption (characterized by covalent bonding).

Lignocellulosic biomass, widely recognized as a potential low-cost source for the production of high added value materials, has been proved to be good precursors for the production of ACs. More specifically, ACs made from biomass are very effective for the removal of metal ions (Kadirvelu et al., 2003; Ho and Ofomaja, 2005; Giraldo and Moreno, 2008), phenols, phenolic compounds (Dabrowski et al., 2005; Dursun et al., 2005), heavy metals and dyes (Ricordel et al., 2001; Chuah et al., 2005) from aqueous solutions. Furthermore, they can adsorb arsenic (As) (Manju et al., 1998) and trace metals (Ahmedna et al., 2004) from drinking water, but also be used as support for noble metals or as catalysts per se in liquid phase reactions (Besson et al., 2005). Activated carbons are also very efficient in the adsorption of nitrate and pesticides from surface waters (Kouras et al., 1995; Murayama et al., 2003; Ayranci and Hoda, 2005; Aslan and Turkman, 2005).

Bromopropylate (isopropyl-4-4′-dibromobenzilate) is a bridged diphenyl acaricide (miticide) effective against all stages of mites such as eriophyidae (eriphyid mites), tenuipalpidae (false spider mites) and tetranychidae (spider mites) (Vial et al., 1971). It kills mites in all postembryonal stages, whether they are susceptible or resistant to chlorinated hydrocarbons and/or organic phosphate compounds (Westigard and Barry, 1970). Bromopropylate was first

considered by Joint Meeting on Pesticide Residues (JMPR) in 1973, and scheduled for periodic review at the 1993 JMPR (ALINORM 93/24A, para93). BP is registered for sale in many countries; however, in Australia it has not been marketed since 1986. Nowadays it is approved for use only in Cyprus, Esthonia and Italy. Nevertheless, Routine Monitoring Programs have shown that BP is one of the most commonly detected pesticide, used even illegally, in some countries among them Greece included. These programs have also discovered that BP residues exceeded the Maximum Residue Limit (MRL), in cases of illegal pesticide use. Except of Greece, residues of BP were also found in France, Belgium and Ireland. Even thought BP is not anymore used in Greece, contamination of waters cannot be avoided due to the trans-boundary waters issued from Bulgaria, Turkey and Albania where BP is still in use illegally. Recently, Greeks scientists (Vryzas et al., 2009) have performed a monitoring study of 147 compounds in surface river waters from northeastern Greece near Greek/Bulgarian/Turkish borders. During 1999–2007, thirteen herbicides and conversion products, as well as thirteen insecticides and conversion products among them BP included, were detected in surface waters of the Evros river basin (North-East Greece).

The mass release for each pesticide applied is calculated as the recommended dose of active ingredient per FU (Functional Unit) in the respective greenhouses during the spring-summer cycle. The IPM (integrated pest management) of BP is 5×10^{-6} kg FU^{-1} (Anton et al., 2004). Its toxicity for humans is very high. The half-lives on plant surfaces for BP were found in literature ranged from 4.5 d (Barba et al., 1991) up to 8.8 d (Joint FAO/WHO, 1993).

The properties and uses of BP are in many ways similar to those of chlorobezilate and chloropropylate. The fields of its application are in apple fruit citrus, stone fruits, grapevines, bananas, strawberries, vegetables, tea, hops and cotton. BP is also used on ornamental plants, artichokes, beans, celery, pineapple, onions, papaya, peaches, peanuts, sugar beet. Moreover, studies have been conducted for the detection and removal of Bromopropylate in beewax and honey (Korta et al., 2001, 2003; Jimenez et al., 2004; Rial-Otero et al., 2007).

The ultimate aim of the present study was the production of low cost activated carbons their eventual use in pesticide removal from waters in rural areas of Greece where there are still some BP residues remaining in surface waters. Collaboration between a Chemical Engineering Department and a Chemistry Department was achieved for the integrated production and use of low cost but high added value materials from biomass. The study comprises two experimental sets. By the first experimental set activated carbons were produced from four different agricultural residues. The production of the ACs performed in the Chemical Engineering Department of Aristotle University of Thessaloniki (AUTH), Greece. In a second experimental set the produced ACs were tested for the adsorption of the acaricide Bromopropylate in the Department of Chemistry, of the University of Ioannina in Epirus (UoI), Greece. A kinetic study was performed for the six ACs (four manufactured from biomass and two commercial ones) in order to estimate the equilibrium time of adsorption and the best fitted kinetic model. Isotherms of BP adsorption were also studied for the four prepared ACs.

2. Materials and methods

2.1. Production of activated carbons

The agricultural residues that were used as precursors for the production of ACs were olive kernels, corn cobs, soya stalks and rapeseed stalks (the abbreviations of the samples in the study are OK, CC, SS and RS, respectively). The raw materials were firstly left to dry in a room temperature, then sieved into smaller particles and milled to 1 mm size and finally dried in a furnace for 24 h at 105 °C.

The experiments were performed in two stages; pyrolysis was performed at 800 °C for 60 min under Nitrogen flow (15 mL min^{-1}) and heating rate 27 °C min^{-1} in order to produce char, then physical activation of char was performed (at the same temperature 800 °C) for 30 min under steam flow (40 g min^{-1}) at 0.5 bar. The experiments were conducted in a batch, laboratory scale, and fixed bed reactor. Experimental facility consists of four main parts: (a) the downdraft fixed bed reactor, which operates at atmospheric pressure, (b) the N$_2$ providing section, (c) the gas cleaning section, and (d) the temperature control section. The reactor was constructed from a 316-stainless steel tube and is surrounded by an individually controlled electric heater that aims at supplying heat for start-up and counter heat losses during reactor's operation. The biomass feeding is batch performed by hand after appropriate dismantling of the reactor tube. At the end of the experiments ACs were pestle into powder and sealed in bottles.

Two commercial activated carbons F400 (Filtrasorb400, Calgon Company) and NORIT® GL50 were used for the comparison with the results of the present study. NORIT® GL50 is a powdered steam activated carbon with an extra fine particle size that can be used in a large range of applications (Zabaniotou et al., 2004).

2.2. Characterization of ACs

The ultimate analysis of the four samples was performed based on the ASTM D 5373-93 "Instrumental Determination of Carbon, Hydrogen and Nitrogen in Laboratory Samples of Coal and coke". A Thermofinnigan CHNS EA1112 Elemental Analyzer was used according to this method, for the determination of carbon, hydrogen, nitrogen, sulphur and oxygen content (by subtraction).

The following standard ASTM methods were used for the proximate analysis of the selected materials. ASTM D 3172 "Proximate Analysis of Coal and Coke" and the related ASTM D 3173 "Moisture in the Analysis Sample of Coal and Coke", ASTM D 3174 "Ash in the Analysis of Coal and Coke" and ASTM D3175 "Volatile Matter in the Analysis Sample of Coal and Coke". Proximate and ultimate analyses of the ACs are presented in Table 1.

ICP analysis was performed in order to record the metals content of the four biomass samples. The analyses were performed in a Perkin Elmer Spectrometer, Optima 4300 DV (Optical Emission Spectrometer). The results of the analysis are also shown in Table 1.

2.2.1. Surface characterization, porosity and pore size distribution

Porous characteristics of the ACs were determined by N$_2$ (−196 °C) and CO$_2$ (25 °C) adsorption isotherms using a Quantachrome volumetric apparatus. Surface area was measured by BET (Brunauer–Emmet–Teller equation) method with the N$_2$ adsorption isotherm over a relative pressure (P/P_0) in the range of 0.05–0.15. Total pore volume, which includes both the micropores and the mesopores, was estimated by converting the amount of N$_2$ gas adsorbed at a relative pressure of 0.99 to liquid volume of the adsorbate (N$_2$). Micropore volumes were determined through the Dubinin–Radushkevich equation (Stavropoulos and Zabaniotou, 2005). Thus, mesopore volume V_{mes} can be determined by the subtraction of the micropore volume from the total pore volume.

Horvath Kawazoe was performed for the pore size distribution using an Autosorb 1 Quantachrome porosimeter. Characteristics of the ACs (commercial and biomass origin) are presented in Table 1, while isotherms are shown in Fig. 1a.

Table 1
Characteristics of ACs.

Sample name	CC	OK	SS	RS	NORIT® GL 50	F400
Ultimate analysis						
C%	76.3	54.73	58.26	59.5	n.a.	87
H%	0.92	1.05	0.8	0.97	n.a.	0.3
N%	4.19	0.46	0.43	0.47	n.a.	0.5
Proximate analysis						
Ash%	9.88	17.35	40.60	26.17	8.95	6.46
Moisture%	6.97	12.94	5.93	8.68	3.92	6.03
FC%	80.72	63.38	46.40	56.21	76.13	73.46
VM%	2.43	6.33	7.07	8.95	10.99	14.05
Metal content (ppm)						
Ca	258	4160	10 400	6400		
K	137	5000	3720	3360		
Na	342	2130	4830	490		
Mg	85	1000	4600	860		
Al	41	760	940	121		
Fe	12	438	500	45.5		
Cu	4.45	37	132	4.5		
Mn	1.13	12	17	7.8		
Ni	0	4.2	4.8	0		
Surface area and porosity characteristics						
S_{BET} (m^2 g^{-1})	630	600	570	490	650	827
V_{ptot} (cm^3 g^{-1} C)	0.34	0.30	0.31	0.28	n.a.	0.52
$V_{micro\ CO2}$ (cm^3 g^{-1} C)	0.34	0.30	0.29	0.21	0.33	0.23
Ref.					(Prasertmanukitch et al., 2004)	(Diamantopoulou et al., 2010)

2.2.2. SEM analysis

The surface morphology of the activated carbons before and after adsorption was performed by a Scanning Electron Microscopy (SEM) JEOL JSM-840A, with a detector of energy dispersion of X-rays.

2.2.3. FTIR analysis

ACs were also analyzed by Fourier Transform Infrared (FTIR) on a Thermo Electron Corporation NICOLET IR200 instrument in order to identify the functional groups that exist on the surface of the ACs. The identification of the peaks was achieved based on literature data (Namasivayam and Kavitha, 2006; Bouchelta et al., 2008).

2.2.4. XRD analysis

X-Ray Diffraction Technique was performed for the characterization of crystallographic structure of the materials. The XRD was a type D500 instrument of Siemens Company with monochromatic light beam scanning Cu K (λ = 1.5406 Å) and scanning velocity 0.05°/s.

2.3. Bromopropylate (isopropyl 4,4′-dibromobenzilate) characteristics

BP (purity 99.2%) (CAS number 18181-80-1, product number 45357-250MG) was the pesticide under study. For the needs of analysis bromophos-ethyl (purity 99.3%) (CAS number 4824-78-6, product number 33399-100MG) was used as internal standard in the gas chromatograph. Both compounds were supplied by the company Sigma Aldrich, Fluka (Germany). BP has 0.1 mg L^{-1} solubility in water and general soluble in organic solvents, as well. General characteristics of BP are shown in Table 2.

2.3.1. Adsorption kinetics

The kinetic study was performed for the six ACs (four manufactured from biomass and two commercial) in order to estimate the equilibrium time of adsorption and the best fitted kinetic model (pseudo 1st and 2nd-order). Inside the centrifuge tubes 0.2g of AC and 40 mL of the aqueous solution 0.5 ppm Bromopropylate were added and shaken in a time range 5–135 min. At the end, samples were centrifuged at 4200 rpm for 10 min. Due to suspension observed after centrifugation; 5 mL of the supernatant solu-

tion was recovered with a pipet and centrifuged again in new centrifuge tubes for another 10 min. Then, the 5 mL of the aqueous phase was extracted twice with 2.5 mL of n-hexane using a Vortex for 1 min. A small amount of anhydrous Na$_2$SO$_4$ was added in into the combined extracts in order to eliminate humidity. After liquid–liquid extraction was accomplished, 50 μL of Internal Standard (IS) were added in each solution (1 ppm bromophos-ethyl) and then chromatographic analysis was performed. The above procedure was repeated for every AC until the maximum removal was estimated.

The percentage of the removal (%) was calculated by following equation:

$$\text{removal } (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

where C_0 and C_e are the initial and the equilibrium concentration, mg L^{-1}.

The two kinetic models used to analyze adsorption data were Legergren's pseudo1st-order and pseudo 2nd-order (Islam et al., 2009):

The two kinetic models were described by the linear curves K_1 and K_2 constants were estimated from the slope of the curves.

The adsorbed amount of the pesticide, q_e, was calculated by following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{2}$$

where C_0 and C_e are the initial and the equilibrium concentration, mg L^{-1}; V is the volume of the solution, mL; m is the amount of AC, g.

2.3.2. Adsorption isotherms

Since equilibrium time was set, the adsorption isotherms of five different Bromopropylate solutions of different concentrations (0.1, 0.25, 0.5, 1 and 2.5 ppm) were studied for each AC sample. The batch sorption experiments were carried out in 50 mL polypropylene centrifuge tubes, where 0.2g of AC and 40 mL of the above pesticide solution were added. The tubes were capped and shaken in a horizontal shaker as long as the equilibrium time of each AC, at constant room temperature (20 °C). The same procedure with cen-
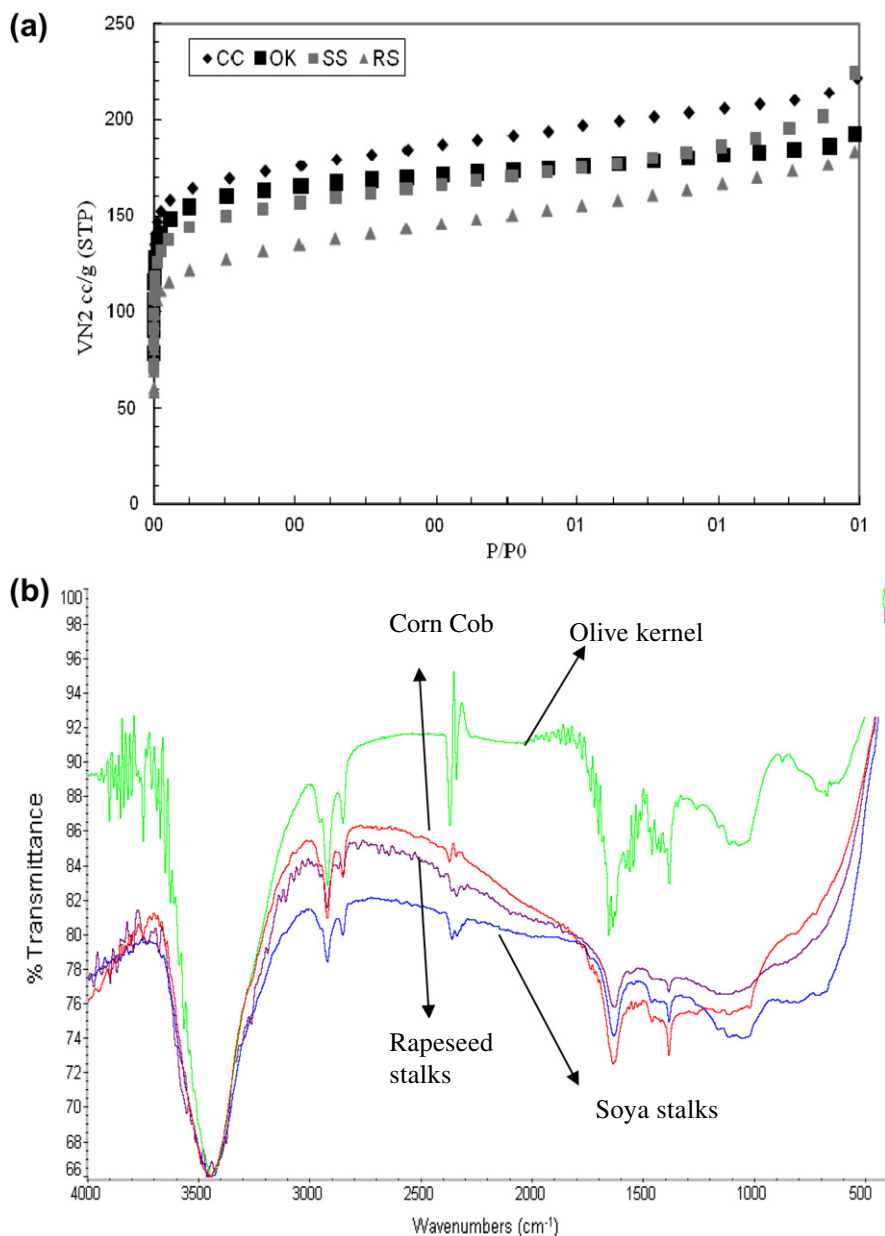
Fig. 1. Characterization of ACs: (a) isotherms of ACs, and (b) FTIR spectra.

trifugation and liquid–liquid extraction, as described above, was performed for isotherms experiments as well.

For the need of adsorption study, two isotherms were applied, Langmuir and Freundlich. The curves for Langmuir and Freundlich isotherms were linear.

Finally, the error function was calculated for each case using following equation:

$$F_{error} = \sqrt{\frac{\Sigma_i^p [(q_{ical} - q_{iexp})/q_{iexp}]^2}{p}} \qquad (3)$$

where q_{ical} is the amount of substance, mg gr^{-1} AC that was calculated; q_{iexp} is the amount of substance, mg gr^{-1} AC that was estimated experimentally; p the number of experiments.

2.3.3. ECD analyses

The gas chromatograph used for the analyses was a Shimadzu 14B, which had an ECD detector (63Ni electron capture) that works at 300 °C and the column was an ADB-1 (J&W Scientific, Folsom,
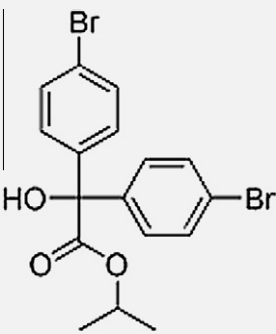
CA, USA). The temperature profile of the method started at 80 °C (2 min hold time) and reached 290 °C (10 min hold time) with a heating rate of 21 °C min^{-1}. The temperature in the injection inlet system was 250 °C. The carrier gas used was He (1.5 mL min^{-1}) and the injection volume was 1 μL. Bromopropylate appeared after 13.1 min, while IS (Bromophos-Ethyl) appeared about 2 min earlier (11.4 min).

As mentioned above, for the needs of the qualitative and quantitative analysis an Internal Standard solution was created, 100 ppm bromophos-ethyl, 50 μL of which was added in every solution before analysis. Furthermore, a second solution was created from both Bromopropylate and bromophos-ethyl in order to be used as Relative Response Factor (RRF). The RRF equation is given by following equation:

$$RRF = \frac{C_A \cdot [AREA]_{IS}}{[AREA]_A \cdot C_{IS}} \qquad (4)$$

where C_A and C_{IS} are the concentrations of Bromopropylate and Bromophos-ethyl, respectively.

Table 2
General characteristics of Bromopropylate (BP).

Structure	Pesticide type	Chemical group	Chemical Formula	M.W.	Solubility in water (mg L^{-1})	Solubility in organic solvents (at 20 °C)
	Acaricide/ insecticide	Benzilate	$C_{17}H_{16}Br_2O_3$	428.13	0.1	High

Toxicity (Anton et al., 2004)			Degradation (Anton et al., 2004)			
Human ADI (kg kg^{-1} d^{-1})	Aquatic NEC (kg m^{-3})	Terrest. PNEC$_{soil}$ (kg kg^{-1}wwt)	Plant DT$_{50p}$ (D)	Air DT$_{50a}$ (D)	Water DT$_{50w}$ (D)	Soil DT$_{50s}$ (D)
3×10^{-8}	1.7×10^{-7}	8.93×10^{-8}	5.9	2.56	3	59
Endpoint LD50 [Symyx® Toxicity database]						
	Guinea pig (oral)	Mouse (oral)	Quail (oral)	Rabbit (skin)	Rat (oral)	Rat (skin)
Dosage (Gm kg^{-1})	3	8	>2	10 200	5	>4

[AREA]$_A$ and [AREA]$_{IS}$ the surface areas of Bromopropylate and Bromophos-ethyl detected on ECD.

3. Results and discussion

3.1. Specific results on ACs characteristics

The ultimate analyses have shown similar characteristics for OK, SS and RS, while CC found to have higher amounts of carbon (Table 1). From the proximate analysis it is clear that CC has the highest amount of Fixed Carbon and lowest amounts of Volatiles and Ash, similar to the commercial ACs. On the contrary, SS and RS have very high amount of Ash and low amount of FC, which is not preferable for AC production. In their high ash content some metal oxides are present, as proved by the ICP analysis, which metal oxides fill or block some portions of micropore volume; this explains partially the low surface area and the high mesoporous volume character observed in carbons with high ash content (Valix et al., 2004; Zabaniotou et al., 2004). The results of this study are in accordance with the results published by Aworn et al. (2008), confirming that biomasses with high ash content, such as SS and RS tend to produce ACs with higher mesopore volumes than the ones with lower ash content, like CC and OK.

As mentioned above, the mineral matter content is one of the most important characteristic of ACs in the adsorption of organic compounds, as it affects the surface area and the porosity of the samples. ICP analysis, presented in Table 1, showed that the principal ash components which are present in high concentrations are Ca, K, Na, Mg and less Al, all of which are essential plant nutrients and soil improvement agents. CC compared with the other materials had the lower amounts of metals. On the other hand SS had the higher values of all metals studied, calcium (Ca) being the first, sodium (Na) magnesium (Mg) and potassium (K) following and final aluminum (Al). OK had the same compounds at high levels lower than SS, except of potassium that was higher. As far as iron concerns, OK and SS showed higher amounts compared with CC and RS. Finally, RS showed high values for potassium and cal-

cium. Sodium, potassium and calcium have catalytic effects on the char gasification reactions, but mineral matter has a negative effect on adsorption properties due to its contribution to the weight of the samples (El-Sheikh et al., 2004).

3.2. Specific results on ACs surface area, porosity and pore size distribution

The surface area, total pore volume (V_{ptot}) and micropore volume (V_{micro} CO$_2$), from CO$_2$ adsorption, are presented in Table 1. As observed, CC was the most microporous material giving the highest BET surface area (630 m^2 g^{-1}) and the highest micropore volume (0.34 cm^3 g^{-1} C) of the four samples. On the contrary, RS gave the lowest (490 m^2 g^{-1}) BET area and the lowest micropore volume (0.21 cm^3 g^{-1} C). The surface area and the microporous area, calculated from CO$_2$ adsorption, had similar trend. OK and SS showed similar surface characteristics and porosity. Generally, it was shown that activated carbons generated from biomass have comparable characteristics with commercial ones.

The above conclusions were also verified by the isotherms. All isotherms (Fig. 1a) at very low relative pressures ($P/P_0 < 0.3$) presented an increase typical of adsorption taking place by filling of micropores classified, as type I (microporous materials). The isotherms exhibited a continuous adsorption increase up to P/P_0 near unity, due to multiplayer coverage at pores greater than 4 nm. Isotherms of CC and OK can be classified as type I of the JUPAC classification for low conversion samples resembling microporous structured materials with slit-shaped pores and extensive development of pore sizes. Isotherms of SS and RS can be classified as type I, but also approach type IV of the JUPAC classification, with weak hysteresis loop, characteristic of microporous materials with some degree of mesoporosity.

Pore size distribution, besides surface chemistry, is the most important characteristic of AC in the adsorption of organic compounds. The accessibility of the organic molecules to the microporosity depends on their size. Pores are classified according to their size into micropores (<2 nm), mesopores (2–50 nm) and macrop-

ores (>50 nm). Pore size distribution is related to kinetic properties of porous material and characterizes the structural heterogeneity of porous materials. All samples had similar pore size distribution, with an increase of numbers of micropores with diameter around 5–6 Å. The largest pores for all samples have a width of about 18.6 Å. This further suggested that the activated carbons prepared were mainly made up of micropores.

3.3. Specific results on SEM

SEM analysis shows the structure and morphological characteristics of the samples. For the classification to hard or soft woody materials SEM pictures were compared with those of micro crystalline cellulose (Oksman et al., 2006) and lignin (Gani and Naruse, 2007) found in literature. Pores in activated carbons are mostly micropores with a less percentage of mesopores. It was observed that hard woody material (like CC and OK) gives cross-interconnected pores spongy like, while softer woody material (like SS and RS) gives fibrous like structure in nature with long ridges, resembling a series of parallel lines (Fig. 2a). Woody materials are composed mostly of lignin, thus their morphology resemble the morphology and structure of lignin. On the contrary softer woody materials, straws, which are composed mostly of cellulose, resemble the morphology of cellulose.

The larger pores contained multiple smaller ones, also noticeable in the straight tubes, which were each with nearly uniform dimensions. In all samples the external surfaces were found covered with smooth open pores of different sizes. Furthermore, due to devolatilization, collisions of these compounds with pore walls might bring about their cracking and carbon deposition (Kumar and Gupta, 1995; Della Rocca et al., 1999; Bonelli et al., 2001), causing the fragmentation and the irregular shapes which were observed. Activated carbons after adsorption showed the same shapes, but more eroded and throttle surfaces than the ones before adsorption.
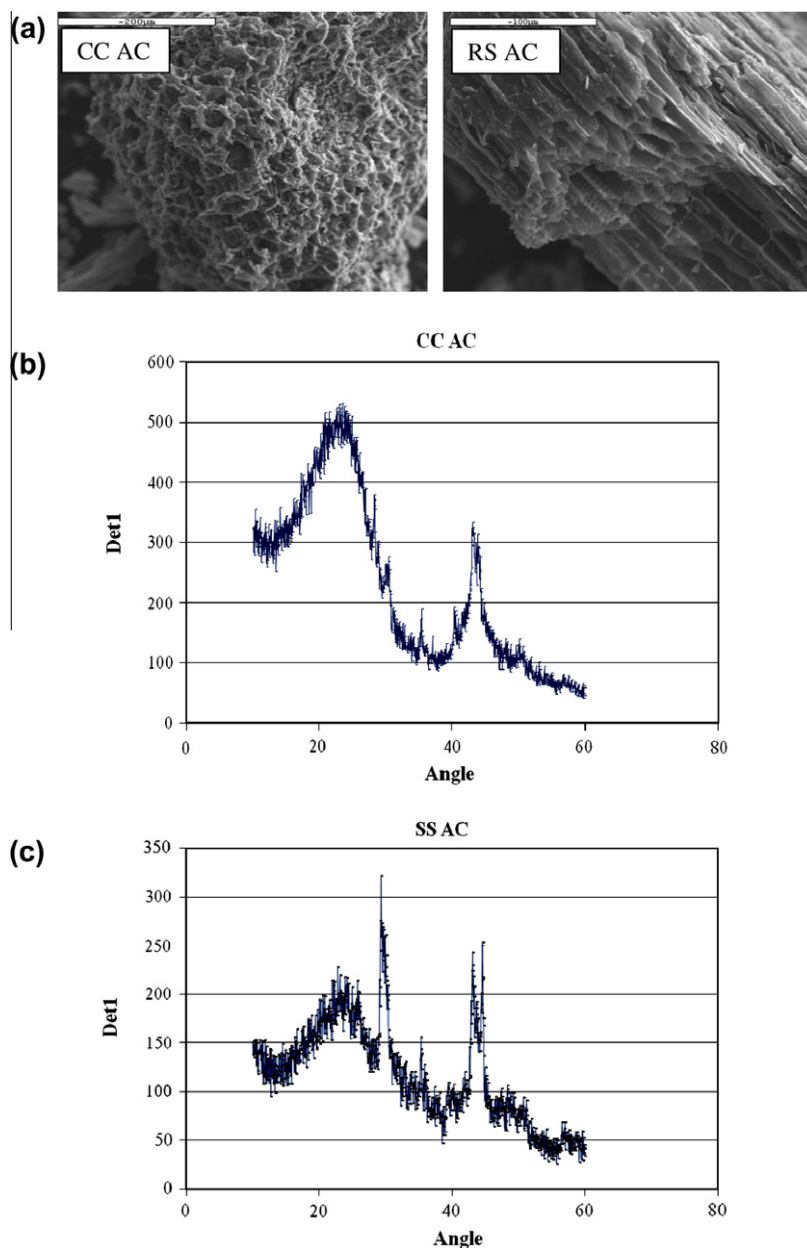

Fig. 2. Characterization of ACs (a) SEM analysis of CC and RS ACs, and (b) XRD analysis of CC and SS ACs.

3.4. Specific results on FTIR analysis

The functional groups that are often observed in ACs in FTIR analysis are alkenes, esters, aromatic, ketones, alcohol, hydroxyl and carboxyl. Similar functional groups were found on the surface of the four biomass ACs (Fig. 1b). Peaks of those groups in the IR analysis appeared at $3400 \, cm^{-1}$, $2950 \, cm^{-1}$, $2850 \, cm^{-1}$, $2350 \, cm^{-1}$, $1650 \, cm^{-1}$, $1300 \, cm^{-1}$, $1480 \, cm^{-1}$ and $1100 \, cm^{-1}$. Accoring to Bouchelta et al., 2008 the peaks that appeared at $3400 \, cm^{-1}$ were assigned to the O—H stretching vibration mode of hydroxyl functional groups including H bonding, at 2950 and $2850 \, cm^{-1}$ indicate the presence of aliphatic C—H stretching, the peak at $2350 \, cm^{-1}$ probably denotes the presence of C=O stretching and at $1650 \, cm^{-1}$ indicates stretching of conjugated C=C or aromatic–oxygen bond in aromatic ether. The bands between 1300 and $1480 \, cm^{-1}$ are assigned to OH bending vibration indicating the presence of phenolic group, or symmetrical bending of C—H bond in methyl group or scissoring vibration of ($—CH_2$) group, which overlaps with methyl group. The band around $1100 \, cm^{-1}$ is assigned to in-plane bending of aromatic ring C—H bond. Finally, a small peak appeared at around $750 \, cm^{-1}$ for CC after adsorption may be due to out of plane ring deformation (El-Sheikh et al., 2004; Namasivayam and Kavitha, 2006). From those groups, the main ones appeared on ACs surface are acidic, thus the carbons are of a basic nature.

3.5. Specific results on XRD analysis

XRD shows a more amorphous nature for CC with smaller peaks comparing to OK, SS and RS which are crystalline like (Fig. 2b). Peaks at 23.5° and 43° were attributed to the presence of carbon and graphite (Bouchelta et al., 2008), while peaks at 24.5°, 29°, 30°, 35° and 42° were attributed to aluminum silicate, calcium silitate hydrate, potassium iron oxide, magnetite and iron oxide, respectively, which was predictable since these specific compounds were found in ash.

3.6. Specific results on adsorption kinetic study

A kinetic study for the six samples was conducted. The two commercial ACs had the same equilibrium time with OK ($t_{eq} \sim 75 \, min$) being the lowest time for reaching the equilibrium, while corn cobs, soya and rapeseed stalks had $t_{eq} \sim 135 \, min$.

Results from the kinetic analysis are shown in Table 3. Pseudo 1st-order model was not applicable as it can be observed, but pseudo 2nd-order was applied successfully to all six ACs, as shown in Fig. 3. According to the high regression coefficient, the adsorptions
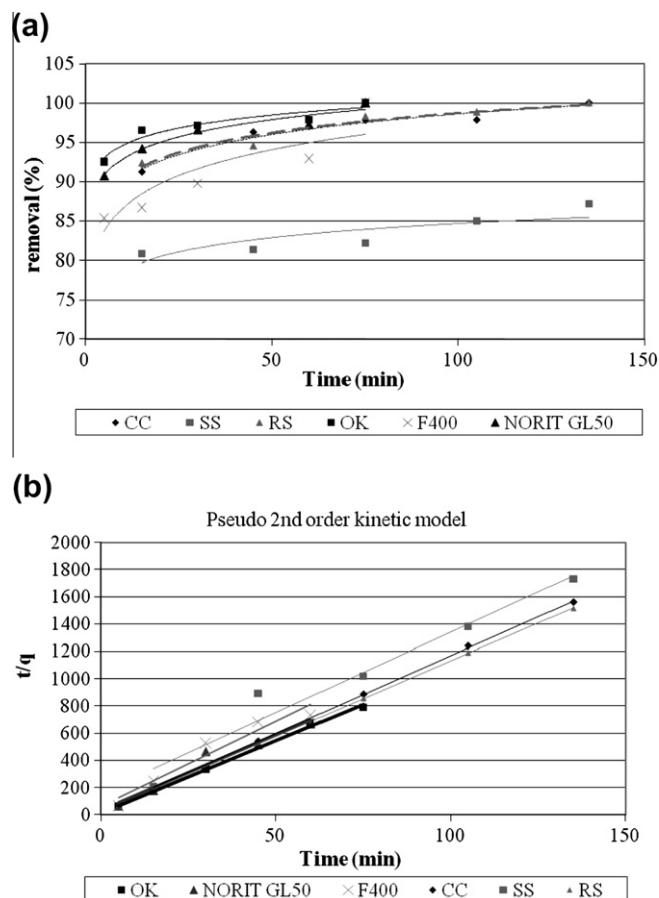

Fig. 3. Kinetic study: (a) BP removal (%) versus time for all ACs, and (b) Legergren's Pseudo 2nd-order kinetics for all ACs.

of BP on the ACs generated from agricultural residues are best fitted by the pseudo-second-order kinetic model compared to pseudo-first-order kinetic model. It is worth to mention that commercial ACs did not have a better behaviour than the manufactured ACs. Bacaoui et al. (2002) who studied olive cake as a precursor for activated carbon production in herbicides removal has also observed that AC with large macropores and micropores showed better adsorption capacities and ability to adsorb herbicides than commercial carbons. Besides, for pseudo-second-order kinetic model the adsorbed amount, q_e is almost equal to the q_e estimated

Table 3
Adsorption kinetic results.

Sample-raw material	Equivalent time (min)	Kinetic constant K_1 (min^{-1})	Q_e Estimated (mg g^{-1})	Q_e Calculated (mg g^{-1})	R^2
Pseudo 1st-order model					
Olive kernel	75	0.0117	0.1403	0.0948	0.6222
Corn cob	135	0.01995	0.142	0.0866	0.8154
Soya stalks	135	0.01677	0.1692	0.078	0.3441
Rapeseed stalks	135	0.0225	0.1383	0.0893	0.949
Norit® GL 50	75	0.01616	0.13867	0.0897	0.0851
F400	75	−0.023	0.1247	0.0817	0.312
Pseudo 2nd-order model					
		Kinetic constant K_2 (g mg^{-1} min^{-1})			
Olive kernel	75	7.56	0.09408	0.0948	0.9972
Corn cob	135	4.28	0.0878	0.0866	0.9998
Soya stalks	135	0.8465	0.0849	0.078	0.9543
Rapeseed stalks	135	4.85	0.0904	0.0893	0.9998
Norit® GL 50	75	3.39	0.0906	0.0897	0.9523
F400	75	2.41	0.08	0.0817	0.9354

Table 4
Langmuir and Freundlich isotherms constants.

| Raw material	Langmuir				Freundlich			
	K_a	q_m	R^2	F_{er}	K_f	n	R^2	F_{er}
Corn cob	26.64	18.9×10^{-2}	0.9952	3.7×10^{-4}	0.77	1.63	0.9107	9.71×10^{-3}
Olive kernel	16.88	12.3×10^{-2}	0.9963	7.42×10^{-4}	0.622	1.46	0.9285	1.53×10^{-3}
Soya stalks	59.44	11.6×10^{-2}	0.9913	5.85×10^{-4}	2.095	0.996	0.9601	3.82×10^{-3}
Rapeseed stalks	106.29	7.9×10^{-2}	0.9993	7.64×10^{-4}	0.659	1.878	0.8886	1.43×10^{-3}
Norit® GL 50	16.73	21.17×10^{-2}	0.9991	9.16×10^{-4}	2.556	0.854	0.8984	1.33×10^{-2}
F400	38.38	15.6×10^{-2}	0.9977	4.97×10^{-5}	0.538	2.779	0.9793	2.34×10^{-3}
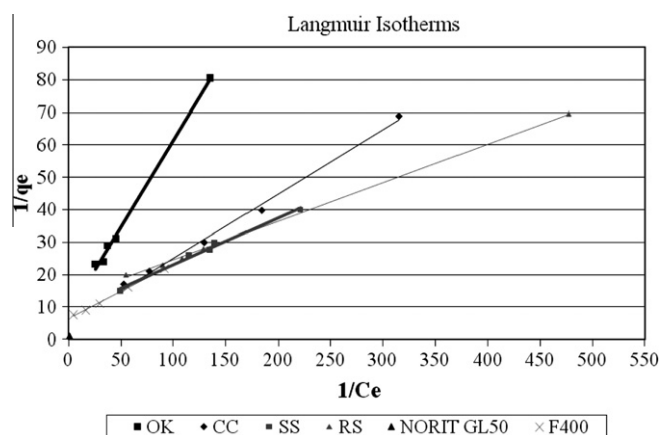
Fig. 4. Langmuir isotherms of BP adsorption on ACs produced from agricultural residues and commercial ACs.

by the experimental procedure (Table 3). Finally, pseudo-second order model suggested that the rate-limiting step might be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate (Ho and McKay, 1999).

3.7. Specific results on Isotherm analysis

The isotherm models that were studied were those of Langmuir and Freundlich, the constants of which are presented in Table 4. All ACs are best fitted to Langmuir isotherm (Fig. 4), even though Freundlich was fitted well enough. For the Langmuir isotherm the regression coefficient was higher and the error function values were lower than Freundlich. The higher value of the maximum adsorptive capacity (q_m) was given by CC, which is considered to be the better AC produced. The next to follow is OK, while the lower q_m, that presented the worst behaviour for BP removal, was RS. This result was somehow expected because of the high percentage of FC and the lower percentage of ash. Furthermore, as mentioned in Section 3.1 ACs produced from CC had lower amounts of metals, thus the negative effect on adsorption is minor. The manufactured ACs OK, SS and RS displayed a satisfactory behaviour, comparing with the commercial F400, while CC had even higher adsorptive capacity (q_m). The microporosity of ACs was the main reason that they were proved suitable for this application. Moreover, CC and OK showed better adsorptive behaviour probably because of the spongy like cross-interconnected pores. The commercial Norit® GL50 had the highest adsorptive capacity for the removal of BP from aqueous solution.

4. Conclusions

In the present work adsorption of a pesticide on activated carbon generated from agricultural residues was studied. The samples that were pyrolysed were corn cob, olive kernels, soya stalks and rapeseed stalks. Pyrolysis chars were subsequently activated with steam. The produced ACs were analyzed by IR, SEM, XRD and from the analyses some important characteristics of the four biomass samples have been revealed. Furthermore, the ACs were tested for the adsorption of an acaricide, Bromopropylate, from aqueous solution. Kinetics and equilibrium studies were performed. For the sake of comparison, two commercial ACs (F400 and NORIT® GL50) were also tested by the same procedure.

The kinetic analysis showed that pseudo 2nd-order model is applicable to all samples, while the equilibrium study showed that the Langmuir model is best fitted the isotherms. The AC with the higher adsorption capacity for Bromopropylate was proved to be corn cob, then olive kernel and soya stalk, while rapeseed stalks gave the lower results for the specific application. The BP removal from water achieved in this study was 90–100% for all ACs for an equilibrium time in the range 75–135 min.

The ACs from biomass residues proved to have similar or even better Bromopropylate removal capacity than the commercial ones (F400 and NORIT® GL50).

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