Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.808845

52 (2014) 4920–4927
July

Taylor & Francis
Taylor & Francis Group

Removal of malathion from polluted water by adsorption onto chemically activated carbons produced from coffee grounds

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Received 15 July 2012; Accepted 7 May 2013

ABSTRACT

The present work is concerned with a comparative study to evaluate the adsorptive properties of activated carbons produced from coffee grounds. Activation was done using different chemical activation agents such as H_3PO_4 and $ZnCl_2$ either separately or mixed together. Characterization of these prepared samples was carried out by determining their physicochemical properties such as specific surface area, porosity, and surface acidity. The results indicated that the produced carbonaceous materials generally developed different and interesting porous structures. Indeed, H_3PO_4-activated carbon (PPAC-P) develops a porous volume of 0.98 cm^3/g and a surface acidity of 317.6 meq/100 g (with a high mesoporous proportion). By contrast, $ZnCl_2$-activated carbon (PPAC-Z) seems to be the most microporous material with a rather limited surface acidity. Adsorption trials with Malathion, a commercial pesticide widely used in Algeria, were carried out onto produced samples of carbonaceous materials in batch experiments at 30°C. Various parameters such as pH, contact time, nature, and amount of adsorbent were investigated for removal efficiency under different operational conditions. Results herein showed that an interesting removal efficiency of 96% was achieved under the following conditions: pH 6, adsorbent amount of 1 g/L, and an equilibrium time of 60 min.

Keywords: Adsorption; Coffee grounds; Active carbon; Pesticides

1. Introduction

Water pollution is a very persistent problem. It is a well-known fact that some organic compounds are highly toxic. Among all organic pollutants, pesticides are considered to be the most hazardous, because of their widespread use and persistence in agricultural land. Consequently, their intrusion into the food chain represents a highly potential health hazard for humans

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and animals. Pesticides and particularly Malathion (widely used in agriculture, Fig. 1) are considered as the very dangerous compounds because of their toxicity and especially their carcinogenic character.

Different treatment techniques have been proposed for water purification. These include chemical oxidation [1,2], biological processes [3,4], photocatalysis [5,6], electrodialysis [7], etc. Nevertheless, the most suitable alternative method remains adsorption [8–11] because of its pollutants' removal efficiency onto adsorbents. Indeed, higher the specific surface area of the adsorbent material used more efficient is the adsorption removal process. Comparatively to other adsorbents, activated carbons are more efficient [12] but their high commercial cost and their difficult regeneration led the investigators to look for less expensive alternatives [13,14].

Various lignocellulosic wastes such as date pits, coconuts shells, olive stones, etc. [15,16] have proved to be interesting raw materials for the preparation of activated carbons. Not only they are good precursors of porous adsorbents, but this operation turns out to be a good means to valorize them. Coffee grounds which is a solid waste, rejected in huge quantities in the environment, seems to have an interesting potential as a starting material for producing activated carbon [17,18]. Basically, there are two different approaches for preparing activated carbons:

- Physical activation which utilizes carbon dioxide or steam as an oxidizing agent at high temperatures (between 800 and 1,100°C). Activated carbon is produced in two steps: the first one is carried out under an inert gas flow and the second one under an oxidizing flow for 24–72 h [19].
- Chemical activation is carried out in one step at lower temperatures (500–700°C) in presence of a dehydrating agent, such as $ZnCl_2$, H_3PO_4, KOH, H_2SO_4, etc. [19,20]. These chemical agents promote the formation of a rigid matrix [21] and can significantly improve pores development.

In the present work, three coffee grounds-based activated carbons were produced by different chemical activation procedures. The main objective was to study the influence of their physicochemical properties on malathion removal effectiveness, as a function of different varying parameters such as time, pH, concentration of adsorbents, etc.

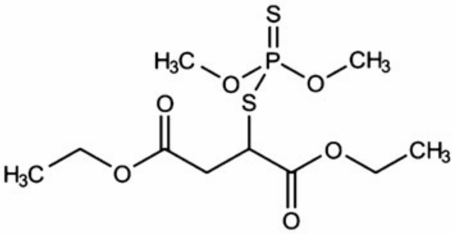

Fig. 1. Chemical structure of malathion.

2. Materials and methods

2.1. Production of activated carbon

Coffee grounds produced locally were used as starting material, after being washed with hot distilled water and dried out at 105°C. For the preparation of activated carbon, chemical activation was performed with different agents: $ZnCl_2$ alone, H_3PO_4 alone, and both of them as a mixture of 50% $ZnCl_2$ and 50% H_3PO_4. Impregnation was carried out by transferring 50 g of coffee grounds into 100 mL of the chemical agent (3 N). Afterwards, the mixture was refluxed at 80°C for 3 h [22] then transferred into a tubular furnace where activation occurred at 600°C for an hour under a nitrogen flow.

Thus, the resulting carbonaceous material was subsequently treated with HCl 0.1 N for 3 h before being washed in a Soxhlet to remove both residual organic and mineral matters. The product was dried at 105°C for 24 h, crushed, and then sieved in order to obtain a uniform material of particle size (30 μm). It was afterwards stored in closed bottles [17].

2.2. Preparation and characterization of activated carbon

2.2.1. Specific surface area

Measurements of specific surface area were performed by nitrogen adsorption at a temperature of 77 K with a Micromeretics volumetric apparatus (ASAP 2010). The specific surface area was determined by application of the Brunauer–Emmett–Teller equation in the range of 0.05–0.35, of relative pressure.

2.2.2. Ultimate composition

Elementary analysis of activated carbons was performed with an elemental analyzer, using a gas chromatography technique. Determination of carbon, hydrogen, and nitrogen contents was were carried out on an Exeter analytical EA 440 analyzer. Oxygen composition was calculated by difference and accuracy was better than 0.7%.

2.2.3. Mineral elements

The mineral composition of elements such as copper, magnesium, cobalt, molybdenum, sodium, phosphor, and zinc was determined by spectrographic analysis (UEI-NICA5 spectrograph) and by X-ray fluorescence (Phillips PW 1480 Sequential spectrometer). Analysis was performed essentially to determine ash contents and to test for the presence of phosphorus and zinc which could originate from the chemical reagent used for activation.

2.2.4. Surface acidity and basicity

Determination of the total acidic and basic surface functional groups (in meq/100 g of activated carbon) was determined according to the protocol established by Boehm [23].

2.3. Pesticide adsorption tests

2.3.1. Adsorption

Pesticide solutions were prepared by adding of 0.1 mg of malathion (Cheminova) to 1 L of bidistilled water. Adsorption experiments were carried out at a constant temperature (30°C) in a batch reactor using a series of 100 mL. Dispersion is kept under stirring to improve external mass transfer. Erlenmeyer flasks were covered with aluminum sheets to prevent contamination. The effect of pH, nature of adsorbent, adsorbent dose, and time were investigated. After optimum contact times, solutions were centrifuged and malathion concentrations in the supernatant were determined.

2.3.2. Pesticide analysis

Centrifuged solutions were analyzed using UV–visible spectrophotometry. Malathion concentrations were determined by measuring UV absorbance at its λ_{max} (195 nm) using a Cintra-5 UV–visible spectrophotometer.

3. Results and discussion

3.1. Activated carbons characterization

Results showed a remarkable specific surface area higher than 900 m^2/g (Table 1) for the prepared activated carbons. Indeed, chemical activating agents promote the formation of cross-links and leads to the formation of a porous structure following heating at high temperatures [21]. Nevertheless, $ZnCl_2$-activated carbon develops the highest specific surface area (1,020 m^2/g) and the biggest pore volume, mainly microporous which could be exploitable in the removal of small pollutant molecules. In addition to that, the role $ZnCl_2$ is to promote aromatic condensation reaction leading to a rigidity of the structure of carbonaceous materials [24].

Table 1
Effect of activating chemical agents on the specific surface area and porosity of coffee grounds-based activated carbon (T, 600°C; time, 1 h)

Chemical agents	A_{sp} (BET) (m^2/g)	V_p total (cm^3/g)	$V_{\mu p}$ (m^3/g)	V_{mes}/V_{Ptot}(%)
$ZnCl_2$	1,020	1.23	0.74	39.83
H_3PO_4	910	0.98	0.32	67.34
$ZnCl_2 + H_3PO_4$	960	1.02	0.41	59.80

H_3PO_4 accelerates cleavage of bonds between biopolymer (principally cellulose and lignin) which is followed by a recombination reaction in a rigid cross-linked structure [25,26]. In fact, phosphoric acid action was studied by different workers [22,27]. According to Bouchenafa–Saib et al. [22], H_3PO_4-activated carbon seems to be more mesoporous with a ratio of approximately 63%. However, when ($ZnCl_2 + H_3PO_4$) mixture is used, activated carbon (PPAC-PZ) seems to be an intermediate product arising from competition between two chemical agents i.e. H3PO4 promotes mesoporous structure (59.8%) whereas $ZnCl_2$ favors microporous structure (40.2%).

Bulk composition of prepared activated carbons is reported in Table 2. All samples showed low nitrogen and hydrogen levels, and high carbon content. However, difference in oxygen content can be seen and it shows that PPAC-P is the most oxygenated material suggesting that its surface acidity is the highest one when compared with the other ones. The difference is probably due to the real composition of the carbonaceous materials themselves, and may be also due to the presence of polyphosphoric species polymerizing at high temperature and not being eliminated by Soxhlet washing.

Results of spectrographic analysis indicate that all PPAC contain very small quantities of copper, magnesium, molybdenum, cobalt, barium, and sodium in the range of 10^{-4}–10^{-2}%. The presence of phosphates was only detected in PPAC-P, suggesting that phosphorus originated from H_3PO_4 activation. On the

Table 2
Bulk composition of different PPAC

Chemical agents	C%	H%	N%	O%
$ZnCl_2$	89.64	2.13	2.47	5.76
H_3PO_4	86.33	1.11	0.99	11.57
$ZnCl_2 + H_3PO_4$	89.76	1.06	1.78	7.40

other hand, low contents of Zn were detected in all samples (less than 10^{-4}%).

Table 3 summarizes global surface acidity ($N^T{}_A$) and basicity ($N^T{}_B$) following sodium hydroxide and hydrochloric acid titration. Maximum acidity was found in H_3PO_4-activated PPAC. Introduction of $ZnCl_2$ led to the decrease of acidity to about 10% which is in agreement with the lower value of surface acidity for PPAC-Z (144.1 meq/100 g), $ZnCl_2$ appears to dehydrate the lignocellulosic precursor at high temperature without creating an important surface acidity. It was also noticed that acidity was strongly correlated to surface oxygen groups [22]. Indeed, an increase of surface oxygen groups enhances the surface acidity as demonstrated by Boehm et al. [23].

3.2. Pesticide adsorption tests

3.2.1. Effect of adsorbent amount and nature

The effect of adsorbent amount (0.1–2.5 g) on the removal of malathion was studied in batch solutions with a contact time of 24 h to ensure equilibrium, at a temperature of 30℃, pH 6, and a malathion amount of 0.1 mg in 1,000 mL of bidistilled water. Results are shown in Fig. 2. Generally, malathion removal yield curve vs. adsorbent dose seems to have the same shape for all the three types. Above 1 g/L of activated carbon, the curve levels off and removal yield remains constant, showing that beyond this value, the adsorbent eliminated all the pesticide present in water. So, the optimum dose of adsorbent is 1 g/L. Nevertheless, as shown, the most important malathion removal yield is obtained on a PPAC-P activated carbon. These results are probably the consequence of two main factors:

Table 3
Surface acidity and surface basicity of different activated carbons

Chemical agents	N_A^T (meq/100 g)	N_B^T (meq/100 g)
$ZnCl_2$	144.1	52.3
H_3PO_4	317.6	48.7
$ZnCl_2 + H_3PO_4$	283.7	49.9

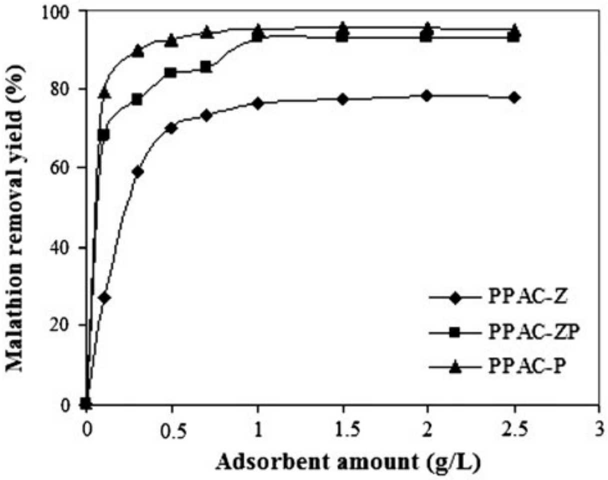

Fig. 2. Effect of adsorbent amount on malathion removal yield for different activated carbons.

(1) The rich functionality of these carbonaceous material groups allows interactions between surface oxygen on one hand and hydrogen and sulfur atoms of the pesticide on the other hand.
(2) The large porosity of PPAC-P favors the insertion of Malathion molecules.

On PPAC-Z, adsorption is weak compared to the adsorption on the first activated carbon. The highest removal yield does not exceed 78%. This is probably due to the fact that there are fewer surface oxygen groups (Table 3) and more micropores in the structure (Table 1), which lead to a mass transfer resistance related to the diffusion into the pore structure [28]. As expected, adsorption on PPAC-ZP is an intermediate stage between those obtained on PPAC-P and PPAC-Z.

3.2.2. Effect of pH

The pH effect on the removal of malathion is presented in Fig. 3. As reported previously, malathion retention depends on the nature of adsorbent.

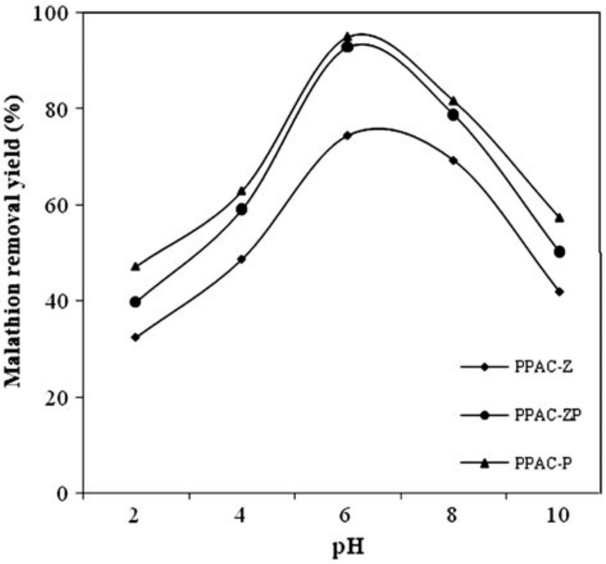

Fig. 3. Effect of pH on the removal of malathion: T, 30℃; m_{PPAC}, 1 g/L; $t_{contact}$, 24 h; and malathion initial concentration, 0.1 mg/L.

Removal by H_3PO_4-activated carbon (PPAC-P) is greater than removal by PPAC-ZP. As mentioned by Imran [29], the pH 6 value appears to be optimal for malathion sorption for all three PPAC. At this pH, H_3O^+ ions are attracted by surface oxygenated groups of PPAC, which could lead to the formation of a bond between H_3O^+ and any one of malathion-sulfur free doublets. Below and above this pH, adsorption is less important which may be explained by an electrostatic interaction between the aromatic structure of activated carbons and the malathion molecule.

3.2.3. *Effect of contact time*

Adsorption kinetics on three activated carbons is presented in Fig. 4. The adsorption of malathion proportionally increases with a contact time up to 60 min. After that time, it becomes constant. This is the time at which the equilibrium concentration of malathion is supposed to be reached. The behavior of PPAC-P is intermediate between those of PPAC-P and PPAC-Z in the time range of 0–55 min. Nevertheless, the adsorption appears better after that time. Indeed, the adsorption yield reaches 76.1, 90.9, and 95.2% on PPAC-Z, PPAC-ZP, and PPAC-P, respectively.

3.2.4. *Adsorption isotherms*

Basically, the adsorption isotherm is an important parameter used to describe how solutes interact with adsorbents. It also allows to optimize the use of adsorbents. The evolution of adsorbed quantity (Q_e) vs. the equilibrium concentration (C_e) at 30˚C (Fig. 5) follows the same behavior for three activated carbons and is related to L model according to Giles classification [30]. The L shape adsorption isotherms shows that there is a low competition between the solvent and malathion to occupy the adsorbent sites surface. This suggests that longitudinal axes of the adsorbed species are parallel to the adsorbent surface as demonstrated by Ignatowicz et al. [31]. It was also shown that the nature of the studied molecule suggests that its adsorption is of the hydrophobic type directly bound to the specific surface of adsorbent particles [32]. The PPAC-P activated carbon seems to be the most efficient when it comes to pollutant retention. The adsorbed quantities are 0.26, 0.12, and 0.10 mg/g for PPAC-P, PPAC-ZP, and PPAC-Z, respectively.

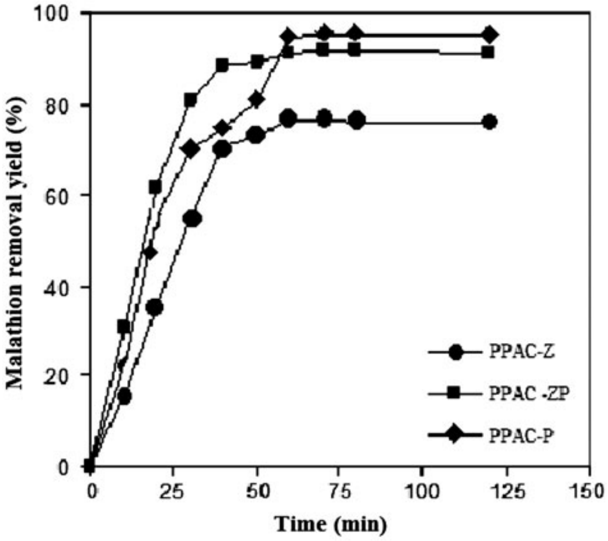

Fig. 4. Effect of contact time on malathion adsorption.

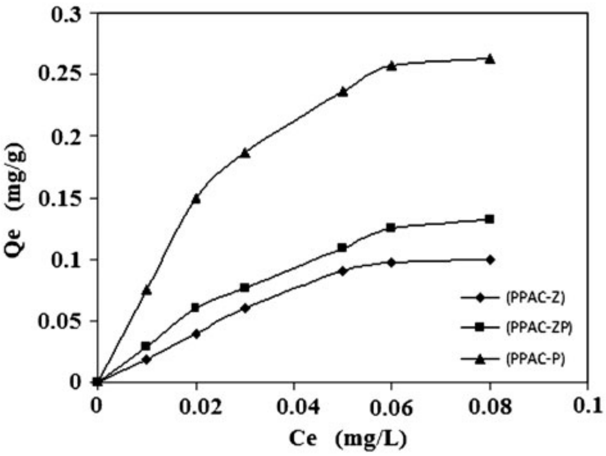

Fig. 5. Malathion adsorption isotherms on different activated carbons.

In addition, the adsorbed quantity of malathion increases with surface acidity as shown in Fig. 6. It

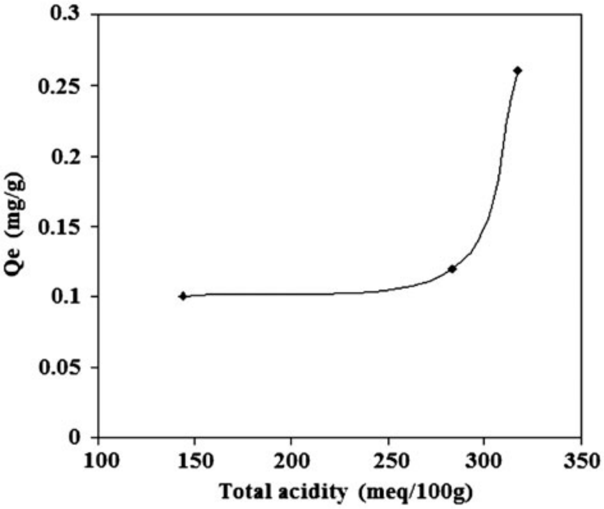

Fig. 6. Influence of surface total acidity of activated carbon on the adsorption capacity.

could be explained by the interactions between peripheral hydrogen atoms (CH_3–O–) and oxygen of acid radicals (–COOH, –OH). The possibility of a tautomeric interaction between the simple bond C–C and the double bond C=S of malathion which would also interact with the peripheral hydrogen atoms cannot be excluded.

Usually, isotherms of the L-model suggest a monolayer adsorption. Evaluation of $1/Q_e$ vs. $1/C_e$ (linearization of Langmuir equation) is illustrated in Fig. 7. It allows determination of Langmuir constants which are summarized in Table 4. Experimental values of Q_m and K lead to a graphical representation of the Langmuir equation in Fig. 8:

$$Q_e = Q_m K C_e / (1 + K C_e) \tag{1}$$

where Q_e—adsorbed quantity; Q_m—maximum adsorbed quantity; C_e—equilibrium concentration; and K—Langmuir constant.

Curves indicate that the monolayer adsorption takes place via the surface free sites. However, microporous PPAC seems to behave differently (at least in the studied range of C_e). In terms of PPAC-Z efficiency, evolution of Q_e vs. C_e is linear, which shows that some adsorption sites remain free. It is not really unusual since Malathion, as a large molecule (length size nearing 1.5 nm), is unable to fully enter microporous cavities.Results obtained with Malathion adsorption were also analyzed by the Freundlich model. The logarithmic form of this model (Fig. 9) is given in the following equation:

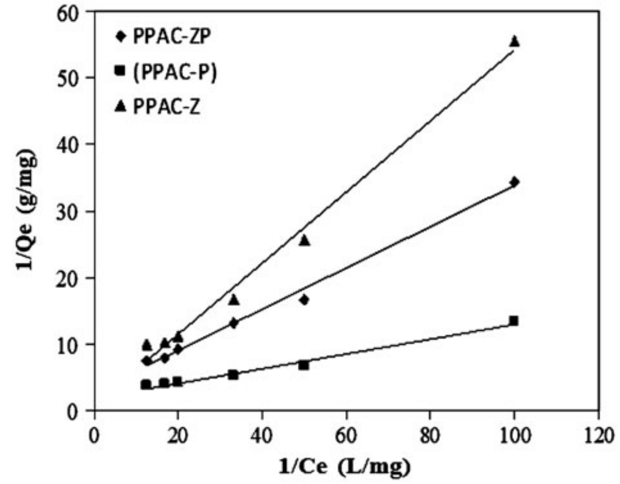

Fig. 7. Evolution of $1/Q_e$ vs. $1/C_e$.

Table 4
Different Langmuir constants values for three activated carbons

	Q_m (mg/g)	K	R^2
PPAC-P	1.168	1.603	0.989
PPAC-ZP	0.348	9.299	0.992
PPAC-Z	0.511	1.764	0.984

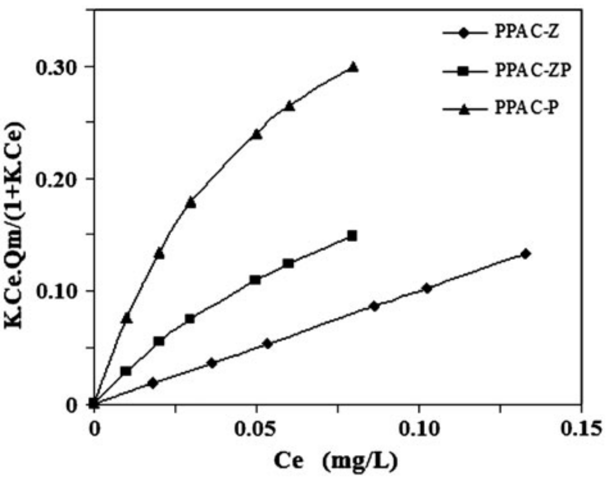

Fig. 8. Evolution of Q_e vs. C_e following Langmuir model.

$$\text{Ln}\, Q_e = \text{Ln}\, K + n\, \text{Ln}\, C_e \tag{2}$$

where Q_e is the amount of adsorbed Malathion (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), K is Freunlich constant related to adsorption capacity, and n is an index comprised between 0 and 1 and related to adsorption intensity [33].

Correlation coefficients are relatively high ($R^2 \geqslant 0.939$) showing a good linearity and the straight lines allow to determine Freundlich constants (Table 5).

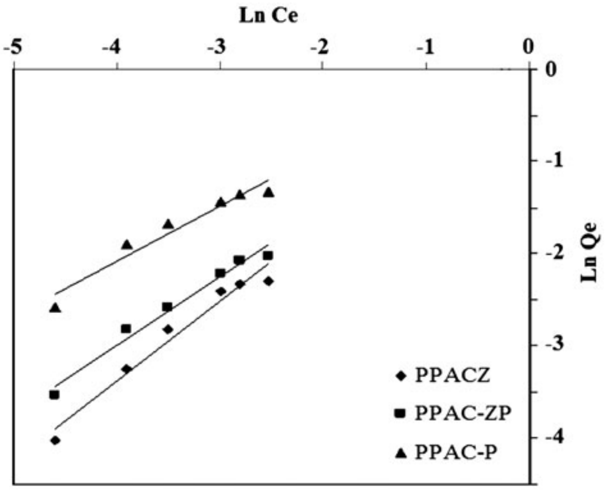

Fig. 9. Evolution of the Freunlich model graph.

Table 5
Freundlich constants values for different activated carbons

Active carbon	*n*	*K*	R^2
PPAC-P	0.599	1.37	0.939
PPAC-ZP	0.734	0.95	0.974
PPAC-Z	0.855	1.05	0.962

The magnitude of the exponent n is comprised between 0 and 1, which confirms the validity of this model. According to Rozada et al. [34], the adsorption is more important when n is smaller. Indeed, it is generally well documented that values of *n* in the range of 0.1–0.5 represent a good adsorption, whereas between 0.5 and 1 a moderately difficult adsorption takes place and over one poor adsorption occurs [35,36]. In addition, it was shown that the adsorption was better on PPAC-P as previously indicated by different workers [37,38]. Indeed, small molecules are well adsorbed on microporous activated carbon while larger pollutants are better fixed on mesopores. In addition, acidity seems to contribute to an increase of the adsorption process.

It is well known that acidity of activated carbons is, on one hand, directly correlated to the surface of oxygen groups, COOH, and OH [22], and that, on the other hand, adsorption rises with an increase of the total acidic number. For this reason, removal of malathion depends on the interactions between the surface oxygen groups of activated carbons and the peripheral hydrogen atoms of Malathion as detailed previously.

4. Conclusion

Physical and chemical properties of activated carbons obtained from coffee grounds were first investigated using two different chemical activating agents ($ZnCl_2$ and H_3PO_4), and their mixture. The use of coffee grounds as precursors for activated carbons production is very promising and the waste usually thrown in discharges could be usefully valorized. Indeed, all activated carbons prepared in this work developed porous structure. They also developed an interesting surface acidity particularly when prepared with phosphoric acid as agent. The malathion adsorption at 30˚C reveals that the optimum pH 6 with an equilibrium time of 60 min for 1 g/L of adsorbent, particularly with PPAC-P (activated carbon prepared with H_3PO_4), can retain about 96% of pesticide. Adsorption follows both Langmuir and Freundlich models. The simplicity of the coffee grounds-based activated carbons preparation method along with the low cost and safety of produced materials make it very promising in the field of pesticides removal efficiency from polluted aqueous media.

Abbreviations

PPAC	—	powdered prepared activated carbon
PPAC-Z	—	$ZnCl_2$ powdered prepared activated carbon
PPAC-P	—	H_3PO_4 powdered prepared activated carbon
PPAC-ZP	—	($ZnCl_2$ + H_3PO_4) powdered prepared activated carbon

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