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# Heavy metals removal by adsorption onto peanut husks carbon: characterization, kinetic study and modeling

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## Abstract

Carbon prepared from peanut husks (PHC) has been used for the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$ , over a range of initial metal ion concentration (0.15 mM). Chemical and physical characteristics of PHC were determined. The effects of particle size and of carbon doses were evaluated by batch experiments. The kinetics of sorption were followed, based on the amounts of metal sorbed at various time intervals. The modeling of kinetic and isotherm curves has also been investigated. The rate constant and the reaction order have been calculated. The results show that  $\text{Pb}^{2+}$  has best affinity to PHC than  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ . From these results an order of the sorption capacity of metal ions sorbed was derived. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Heavy metals; Kinetic adsorption; Peanut husks; Characterization; Modeling

## 1. Introduction

Heavy metals are nowadays among the most important pollutants in surface and groundwater. They are extremely toxic elements, which can seriously affect plants and animals and have been involved in causing a large number of afflictions [1]. Levels of heavy metals in the environment have increased due to pollution caused by industries [2,3]. Therefore, the elimination of heavy metals from water is important to protect public health. Treatment processes for metals contami-

nated water include chemical precipitation, membrane filtration, ion exchange, carbon adsorption and co-precipitation/adsorption [4]. Over the last few years, adsorption has been shown to be an economically feasible alternative method for removing metal ions in water [5,6]. Activated carbon has been an effective adsorbent [7]. The adsorption of metal ions on carbon containing materials such as lignite, wood bark and charcoal has been thoroughly studied over the past two decades. Many reports have appeared on the development of activated carbon from cheaper and readily available materials. Throughout the world agricultural by-products, such as rice husks [8] or coconut shell [9] are some of the raw materials used in activated carbon production. Inexpensive,

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effective, readily available materials can be used in place of activated carbon or ion exchange resins for the removal of heavy metals from solutions. Modified groundnut husks [10,11], sphagnum moss peat [12] and brown seaweed bio-mass [13] were used in the sorption of heavy metal ions. A review of potentially low-cost sorbents for heavy metals has been recently reported [14]. Peanut husks widely available in Senegal are of little or no economic value and in fact present a disposal problem. The vast quantity of waste is generally dumped in landfills. They can undergo a thermal valorization. The resulting peanut husks carbons (PHC) are in appearance of a similar structure to activated carbons and consequently could be used as adsorbent. PHC may contain polar functional groups such as aldehydes, ketones, acids and phenols. These groups could be involved in chemical bonding and would be responsible for the adsorption capacity of the PHC. Thus, a project of PHC valorization was started on the adsorption of heavy metals (Pb, Zn, Ni, Cd) in aqueous solutions. In our case, the crude material was provided by National Company of Oilseeds Marketing of Senegal (SONACOS). The quantity of PHC provided by the company has been estimated to 10000 tons in mean per year. In this work, analyses and batch adsorption experiments have been carried out to characterize and to understand adsorption mechanism by modeling the adsorption kinetic. The aim of the present paper was to study the possibility of the removal of metal ions by PHC as well as the effects of particle size and of carbon dose. A kinetic study according to three different models has been applied. Using batch studies, the rate constants and the reaction order have been calculated.

## 2. Materials and methods

### 2.1. Adsorption materials

#### 2.1.1. PHC preparation

Starting PHC is prepared in same way for all the experiments in order to reproduce results and to ensure homogeneous samples. The material

was rinsed with distilled water, dried at 100°C, and sieved to 0.8–0.5 mm size. Then, the pH was adjusted with 0.1 N HCl at values between 6 and 7. After separation, PHC was dried and stored in an oven at 80°C.

#### 2.1.2. Mineral composition

Metals as Al, Fe, and Si, alkaline as K and Na, alkaline-earth as Ca were determined. A sample of PHC was put in an oven at 900°C for 15 h. All the metal elements were changed in their oxide form. Afterwards, the remaining sample was dissolved in a 70:30 HF/HCl acid mixture for the determination of Ca, Fe, K, Na and in an alkaline solution (NaOH) for the analysis of Al and Si. The solutions obtained were filtered then subjected to atomic absorption spectroscopy using a Varian model 1275 Atomic Absorption Spectrophotometer (AAS), with an acetylene–air flame for Ca, Fe, K, Na and a nitrogen protoxide–acetylene flame for Al and Si. Estimation of each ion was performed using their principal wavelengths. A calibration curve was prepared recording the absorbance of standard concentration solutions of each ion. The absorbance of a sample was measured and the concentration was calculated from the calibration curve.

#### 2.1.3. C, H, N, O dosage

Elemental analysis was carried out with an C.H.N. 1106 Carlo Erba MicroAnalysing device equipped with inductive furnace analyzer. A sample of PHC was put in an oven at 1000°C under oxygen in order to obtain a quick and complete combustion. N<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> were released and conducted in a copper oven at 650°C, then passed through a 2 m column with helium vector gas, and analyzed by a catharometer detector.

#### 2.1.4. Functional groups dosage

In order to know the surface acidity, neutralization techniques with selective bases were carried out according to Boehm method. Neutralization of solutions of NaHCO<sub>3</sub> (0.1 M), Na<sub>2</sub>CO<sub>3</sub> (0.05 M), NaOH (0.1 M) and C<sub>2</sub>H<sub>5</sub>ONa (0.05 M) by carbons was followed. For that

purpose, four samples of 0.5 g portions of PHC were mixed with 50 cm<sup>3</sup> of the respective solution. The solutions were shaken by means of a magnetic agitation for 72 h. Then, the solutions were filtered and 10 cm<sup>3</sup> of filtrate were taken and dosed with chlorhydric acid 0.1 N using helianthin for NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>, phenolphthalein for NaOH and C<sub>2</sub>H<sub>5</sub>ONa.

Surface basicity was also evaluated by calculating the decrease in concentration of a 0.1 M solution of HCl mixed with 0.5 g of carbon. A sample of 0.5 g of PHC was mixed with 50 cm<sup>3</sup> of chlorhydric acid solution 0.1 N. The solution was shaken by means of a magnetic agitation for 72 h. After filtration, 10 cm<sup>3</sup> of filtrate were taken and dosed with NaOH 0.1 N in the presence of phenolphthalein.

### 2.1.5. Infrared (IR) spectra

Infrared (IR) spectroscopy has received much problem due to the difficulty of obtaining data on these highly opaque samples. To obtain the optimum absorption spectra, the PHC was ground to a very fine powder form in a agate mortar for a minimum of 10 min. After drying at 100°C for at least 2 h, dilution and homogenization to 0.05% (w/w) with KBr (spectroscopic grade) were carried out with additional grinding. Discs (25 mm diameter and approx. 1 mm thick) were pressed in a vacuum KBr press. The transmission FTIR Spectra were measured using a spectrophotometer Nicolet 205 and recorded with a varying number of scans and resolutions. The absorption spectra (2500–600 cm<sup>-1</sup>) were then collected and analyzed.

### 2.2. Metals solutions

All the Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup> and Cd<sup>2+</sup> solutions were prepared using PbCl<sub>2</sub>, ZnCl<sub>2</sub>, NiCl<sub>2</sub>·6H<sub>2</sub>O, and CdCl<sub>2</sub> purchased from Labosi or Prolabo, to give metal ion concentrations of 0.15 mM. All solutions were made in distilled water at pH 6. A control sample was taken before each experiment to determine the exact metal concentration before contact with PHC. The solution concentration was determined using AAS under an acetylene–air flame.

### 2.3. Adsorption experiments

Adsorption assays of the different metal ions on the PHC were performed in 1000 cm<sup>3</sup> Erlenmeyer flasks. About 800 ml of the metal solutions was added to the flask already containing PHC. At first, the reaction time was varied in order to determine the time of equilibrium, which has been found to be 2 h. After all, the solutions were shaken for 2 h by means of a magnetic agitation at 300 rpm. Temperature was maintained at 20 ± 1°C. Samples of 5–10 cm<sup>3</sup> of solutions were taken at 1, 5, 10, 20, 40, 50, 60, 80 and 120 min. They were filtered, diluted (if necessary) and analyzed by AAS. The quantity of adsorbed metal ion on PHC was calculated as the difference between initial concentration and concentration at equilibrium. Experimental results and discussion

## 3. Characterization of PHC

### 3.1. Porosity and surface area

#### 3.1.1. Porosity and surface area

Pore-size distributions and the apparent surface area were determined by N<sub>2</sub> volumetric adsorption using a Coulter SA 3100 volumetric gas adsorption analyzer by applying the Brunauer, Emmett and Teller (BET) method to the N<sub>2</sub> isotherm [15]. Nitrogen adsorption isotherms were determined at 77 K. For this, a gas N<sub>2</sub> comes into contact with the PHC in order to obtain a monolayer surface. The software determines the volume V<sub>m</sub> (cm<sup>3</sup>) of adsorbed gas, and calculates the surface area S<sub>BET</sub> (m<sup>2</sup> g<sup>-1</sup>) using the relation:

$$S_{\text{BET}} = \frac{N_{\text{A}} \cdot V_{\text{m}} \cdot S_{\text{m}}}{V_{\text{M}}}$$

where N<sub>A</sub> is the Avogadro number, S<sub>m</sub> the area filled with one molecule adsorbed on the surface of the solid and V<sub>M</sub> the gas molar volume. The results of porosity and surface area analyses are represented in Table 1.

The surface area of PHC has been found equal to 485 m<sup>2</sup> g<sup>-1</sup>. This value is very high in comparison with other carbons which have a surface area about 10–100 m<sup>2</sup> g<sup>-1</sup>. Elsewhere, PHC remains

as a crude material and it was used without activation. Moreover, as can be seen from Table 1, most PHC have areas of pores whose diameters were less than 3.5 nm. It seems that the PHC used were also microporous.

### 3.1.2. Microscopic structure

In order to know the structure sight of PHC, morphological analysis of the PHC was performed by scanning electron microscopy (SEM) using a Zeiss DSM 960 microscope. The working tension was 12 kV. Samples were prepared where sample powders deposited on the support and metallized with gold. The morphological appearance of the PHC is shown in Fig. 1. Photograph I

represents the surface of a crude PHC grain without metal adsorption. Different pore sizes may be observed. Photograph II shows the surface of a PHC grain, which had adsorbed  $\text{PbCl}_2$  depicting the different patterns of metal crystal formed.

### 3.1.3. Chemical composition

The results are shown in Table 2. Values are expressed as percent w/w. As can be seen, PHC is a complex heterogeneous material composed mainly of carbon and silicate. The chemical composition of N, Ca, Na, K, Al and Fe is very low. It can be noted that PHC has 16% of oxygen. The total percentage is slightly above 100 due to the additive experimental errors.

Table 1  
Porosity and surface area of PHC

Diameter of pores (nm)	Volume of pores ( $\text{cm}^3 \text{g}^{-1}$ ) $\times 10^{-3}$	Volume (%)	Area of pores ( $\text{m}^2 \text{g}^{-1}$ )	Area (%)
<3.5	230.90	93.23	478.0	98.48
3.5–6	5.59	2.26	5.1	1.05
6–8	1.54	0.62	0.7	0.14
8–20	3.69	1.49	1.1	0.23
20–80	3.95	1.59	0.4	0.08
80–128	2.00	0.81	0.1	0.02
Total	247.67	100	485.4	100

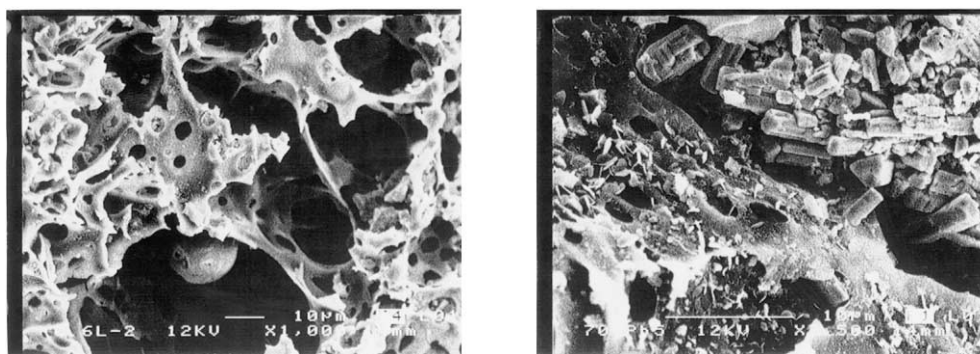


Fig. 1. SEM photographs of PHC in a crude form (Photography I) and in adsorbed form (Photography II).

Table 2  
Chemical composition of PHC

Elements	C	H	O	N	Ca	Na	K	Al	Fe	Si
%	56	1	15.8	0.5	1.2	2.7	2.6	1	1	20

Table 3  
Results of dosage of acid and basic functions of PHC

Functional groups	(meq g <sup>-1</sup> )
Carboxyl groups (I)	0.63
Phenolic hydroxyl groups (II)	0.52
Carbonyl groups (III)	0
Lactone groups (IV)	0
Total of functions of acid surface	1.15 (2.37 meq m <sup>-2</sup> ·10 <sup>-3</sup> )
Total of functions of basic surface	0.35 (0.72 meq m <sup>-2</sup> ·10 <sup>-3</sup> )

### 3.1.4. Functional groups

Knowing the chemical structure of the used carbon is important to understand the adsorption processes. The adsorption capacity of carbon is strongly influenced by the chemical structure of their surface. The surface structures of carbon–oxygen (functional groups) are by far the most important structures in influencing the surface characteristics and surface behavior of carbon. The functional groups suggested most often are carboxyl groups (I), phenolic hydroxyl groups (II), carbonyl groups (e.g. quinone-type) (III), and lactone groups (e.g. fluorescein-type) (IV).

The functional groups depend on the temperature of the preparation of carbon. Table 3 shows the result of acid and basic functions of PHC. As can be seen, the total of acid functions is more important than the total of basic functions and this material contains neither strong carboxylic acid nor carbonyl nor lactone functions.

### 3.1.5. Infrared spectroscopy

The band assignments were made based on the model compounds and the types of functional groups known in organic chemistry [16]. The transmission FTIR spectra of the PHC before and after Ni<sup>2+</sup> adsorbing are shown in Fig. 2a and b. As can be seen in Fig. 2a, the absorption bands observed in the region 1000–1250 cm<sup>-1</sup> occur with the broadest, the strongest overlapping bands involving the stretching vibrations of the C–O bonds. It has been also noted by several authors using different carbon materials [17,18]. These absorptions most probably arise from the phenolic structure. The 1360–1380 cm<sup>-1</sup> band

may be attributed to the aromatic CH and carboxyl-carbonate structures [19]. The 1700–1760 cm<sup>-1</sup> region together with that at about 2400–2450 cm<sup>-1</sup> are characteristic of the carboxylic acid groups referring to the IR spectra of carbons of other works [20,21]. If the spectra of PHC before (Fig. 2a) and after (Fig. 2b) adsorption were compared, it is seen that the main adsorption band centered near 1100 cm<sup>-1</sup> had largely diminished while the 2400–2450 cm<sup>-1</sup> band had completely disappeared.

The spectra presented and the base neutralization results described above, indicate that the main surface oxides were found to be phenols and carboxylates which agreed with most investigations on carbon materials in the literature. Other postulated groups may be included, but the PHC used was crude carbon not activated carbon.

### 3.1.6. Other chemical-physical characteristics

Characteristics of the PHC such as pH solution, bulk density, ash content, moisture content, solubility in water (inorganic and organic matter) were determined. The pH was measured in a suspension of 1 g of PHC in 1 l of distilled water after a contact time of 24 h at 25°C. The ash content was determined by burning it in a furnace at 900°C. The density was obtained using apparatus based on displacement of CH<sub>2</sub>Cl<sub>2</sub> at 25°C according to the Archimedes' principle. The results are summarized in Table 4. It is important to note the high ash content of the PHC. The conductivity is weak in agreement with the value of pH, which is close to neutrality. The leaching of carbon, chloride and sulfate ions is low in accordance with the leaching of activated carbons [5].

## 3.2. Kinetic study

### 3.2.1. Particle size effect

PHC particle size is an important factor in adsorption kinetics because it determines the time required for transport within the pore to adsorption sites. When the same carbon dosage was used, the equilibrium time is less for smaller size, which can reduce significantly the carbon usage rate.

A sample of PHC was sieved to various sizes (greater than 1.25, 1.25–0.8, 0.8–0.5, 0.5–0.25, less than 0.25 mm of diameter) in a Rota-Lab sieve. The particle size effect was studied on the removal of 0.15 mM  $\text{Cd}^{2+}$  solution with 1 g of PHC in 1 l Erlenmeyer flask. Results of the sieving of the PHC sample and the measured values of the residual concentration of  $\text{Cd}^{2+}$  in solution at various times relating to various sizes are represented in Tables 5 and 6. The  $Q$  values expressed in  $\text{mmol}\cdot\text{g}^{-1}$ , derived from concentration, are calculated and plotted versus time in Fig. 3.

As can be observed in Table 5, main of the PHC sample has a particle size greater than 0.25 mm.

The PHC sample looks more like grain than powder. Fig. 4 shows the results of the effect of particle size on the removal rate of  $\text{Cd}^{2+}$  which increases with time and reaches equilibrium after 2 h. The removal of  $\text{Cd}^{2+}$  was not effective for the grain whose diameter was less than 0.25 mm. The adsorption rate was significantly reduced. As has been observed experimentally, one can attribute this result to the inadequate agitation rate and/or the difficulty of hydration.

The diameter of grains, which was between 0.25 and 0.5 mm, shows an effective removal. It was not, however, effective to have grain whose diameter was greater than 1.25.

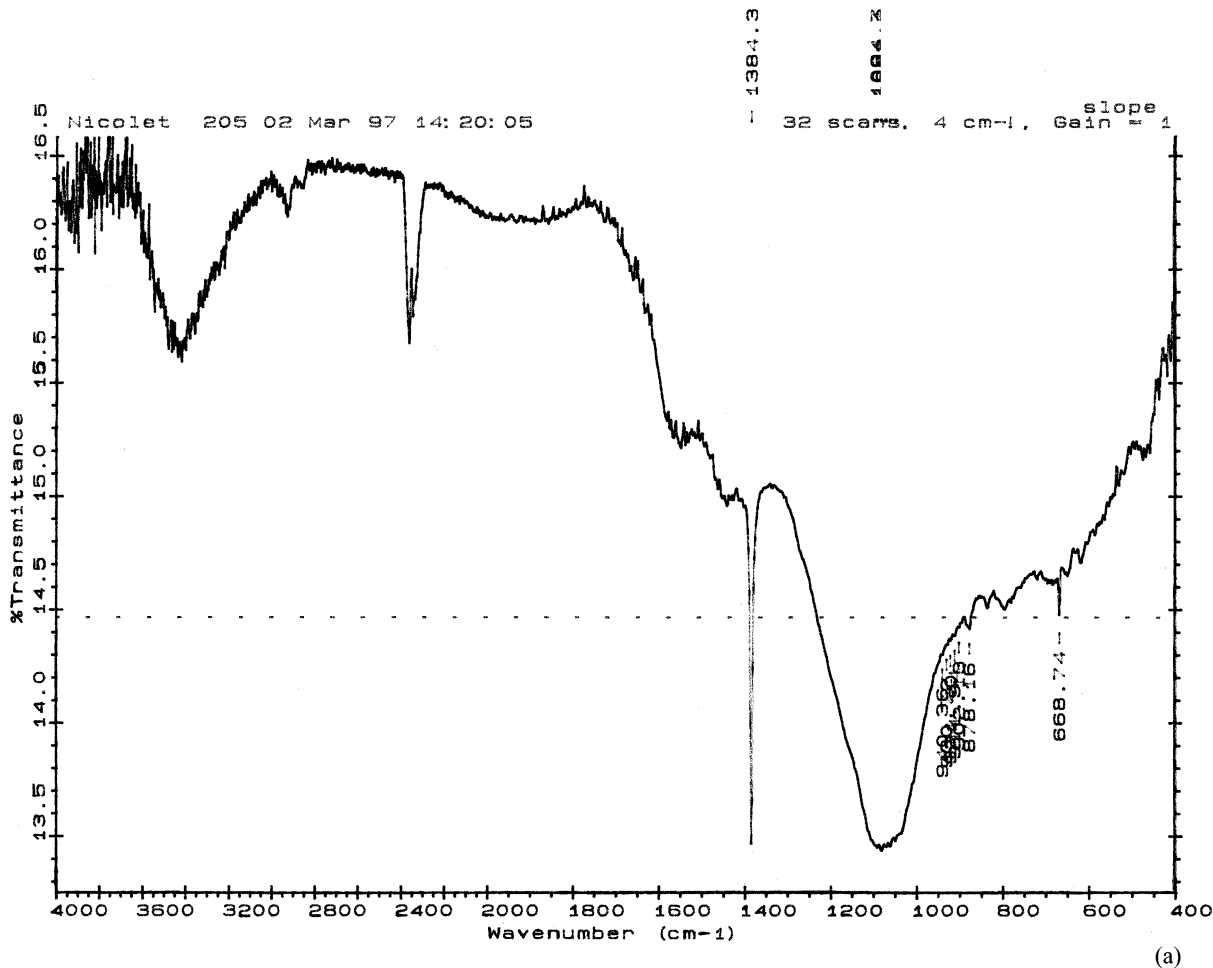


Fig. 2. FTIR spectra of PHC in a crude form (a) and in adsorbed form (b).

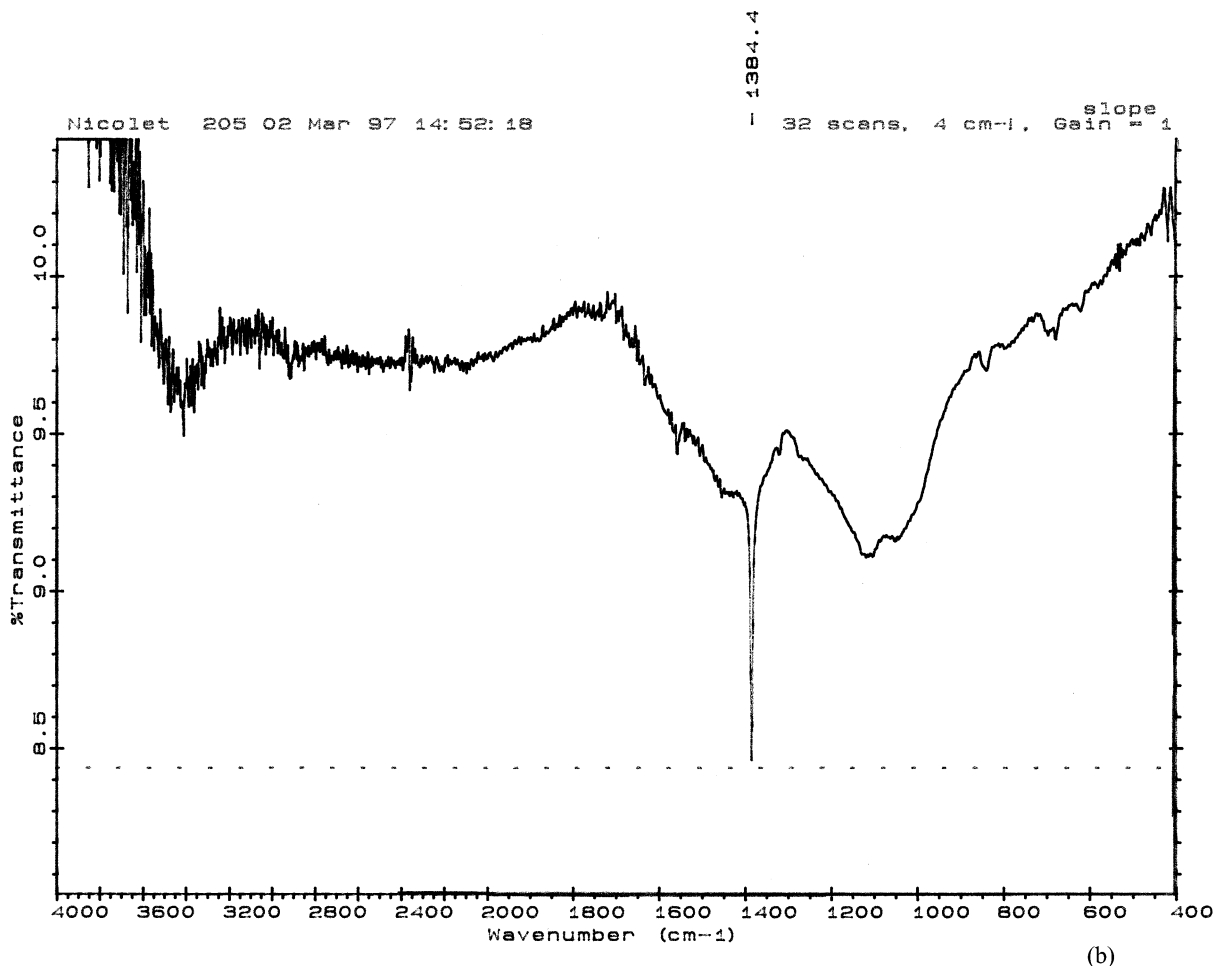


Fig. 2. (Continued)

In order to have, for all the following experiments, a sufficient and an homogeneous sample, a mixture of grains with diameters between 0.25 and 0.8 mm was taken.

### 3.2.2. Effect of carbon dose

The effect of adsorbent dose was studied using a 1 l solution of 0.15 mM of  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$  and PHC with amounts varying from 50 to 1500 mg. The results are represented in Figs. 4 and 5. As can be observed in Fig. 4, quantitative removal of  $\text{Pb}^{2+}$  requires a minimum carbon dosage of 500 mg PHC to reach equilibrium when 1000 mg are necessary to the removal of  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$ . This indicates that the PHC

exhibits preferential adsorption of different metal ions from aqueous solution.

Table 4  
Chemical-physical characteristics of PHC

Parameters	PHC
Moisture (%)	16
Ash (% at 900°C)	21
Conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	6
Density	1.3
Carbon leaching (%)	5
pH	6
Anions leaching (%)	$\text{SO}_4^{2-}$ 0.7 $\text{Cl}^-$ 2

Table 5  
Particle size distribution of PHC

Diameter (mm)	% mass
> 1.25	10.15
1.25–0.8	25.70
0.8–0.5	27.35
0.5–0.25	23.10
<0.25	13.70

Fig. 5 shows the rate of removal of  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$  and  $Ni^{2+}$  from initial solution concentrations of 0.15 mM for each element with 1000 mg PHC dose. As can be seen for all elements, the adsorption rate increases with time and reaches a maximum after 2 h. Adsorption is relatively rapid with mostly dissolved metals being removed from solution within 40 or 60 min contact time. It can be observed that the  $Pb^{2+}$  was the most rapidly removed from solution, followed by  $Zn^{2+}$  and  $Ni^{2+}$  and finally  $Cd^{2+}$  which was adsorbed the most slowly. Furthermore, the adsorbed quantity of  $Pb^{2+}$  was more important. In excess of 98% of  $Pb^{2+}$  were removed, 87, 83 and 75% removal have been found in the case of  $Zn^{2+}$ ,  $Ni^{2+}$  and  $Cd^{2+}$ , respectively.

Thus, the amount of metal ion adsorbed at a

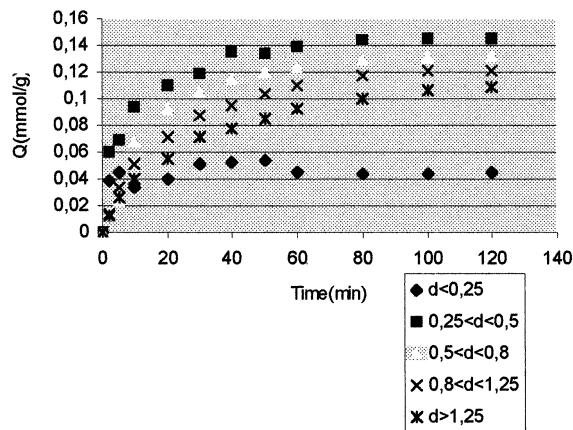


Fig. 3. Adsorption kinetic of  $Cd^{2+}$  according to different particle size; evolution of the adsorbed quantity  $Q$  ( $mmol\ g^{-1}$ ) in relation to time.

given equilibrium concentration increases in the order  $Cd^{2+} < Ni^{2+} < Zn^{2+} < Pb^{2+}$ , which might be explained on the basis of their ionic radii, hydration energy, ionic mobility and diffusion coefficient. All these properties parameters are taken from [21,22] and given in Table 7. Hydration energy is an important parameter to take into account since that the hydrolysis of metal ions occurs by the replacement of water ligands in the inner coordination sphere with hydroxo groups.

Table 6  
Adsorption kinetic of  $Cd^{2+}$  according to different particle size: measured values of the concentration of  $Cd^{2+}$  in solution ( $mg\ l^{-1}$ ) at various times

Time (min)	Concentration of $Cd^{2+}$ in solution ( $mg\ l^{-1}$ )				
	<0.25	0.25–0.5	0.5–0.8	0.8–1.25	> 1.25
0	16.53	16.53	16.53	16.53	16.53
2	12.13	9.79	14.85	15.03	15.13
5	11.51	8.75	13.79	12.79	13.62
10	12.71	5.98	8.88	10.73	12
20	11.99	4.22	6.16	8.56	10.28
30	10.83	3.23	4.71	6.69	8.57
40	10.6	1.41	3.6	5.82	7.84
50	10.52	1.43	3.07	4.92	6.99
60	11.52	0.92	2.6	4.23	6.15
80	11.55	0.39	2.1	3.33	5.29
100	11.6	0.28	1.83	2.95	4.52
120	11.52	0.22	1.7	2.83	4.26

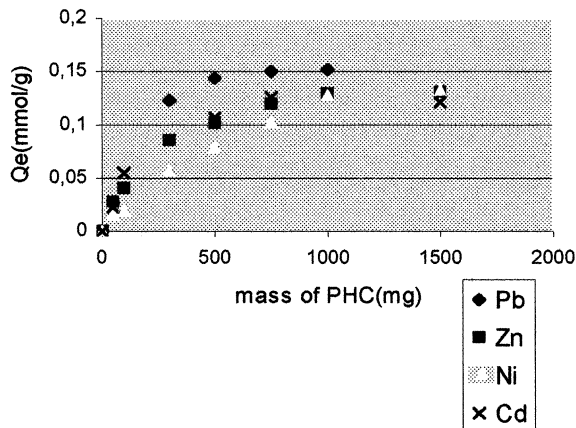


Fig. 4. Adsorption kinetic of  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$  and  $Cd^{2+}$ : evolution of the adsorbed quantity at equilibrium  $Q_e$  ( $mmol\ g^{-1}$ ) for each element in relation to the carbon dose.

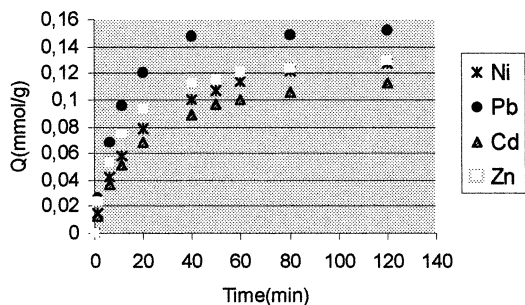


Fig. 5. Adsorption kinetic of  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$  and  $Cd^{2+}$ : evolution of the adsorbed quantity  $Q$  ( $mmol\ g^{-1}$ ) for each element in relation to time.

Adsorption may be related directly to the loss of the outer hydration spheres that precedes hydrolysis. According to these parameters values,  $Pb_{aq}^{2+}$  ions will have a greater accessibility to the surface of certain pores than the other metal ions, which

would lead to a higher extent in the adsorption process. The same order has been found by other authors using different raw materials [23], granular activated carbons [24] or blast furnace sludge [25]. The explanation of the first authors was given on the basis of the surface covered by the adsorbed metal ions, when the latter authors have explained their results on the basis of the metal surface complexation constants and thermodynamic parameters values, respectively.

The lower extent in the adsorption of  $Cd^{2+}$  with regard to  $Pb^{2+}$  might be due to its smaller polarizing power. Thus, the carbon- $Cd^{2+}$  interaction forces will be weaker than those corresponding to  $Pb^{2+}$  and,  $Cd^{2+}$  will be retained only on those surface centers with a density of negative charge higher than that necessary to retain  $Pb^{2+}$ .

These preliminary results show that PHC is an effective adsorbent for the removal of metal ions from aqueous solutions. Its capacity is much superior to the commercial activated carbon as has been compared with the findings of other authors [1,24,26]. It would be useful for the economic treatment of wastewater. The difference in binding capacity is useful in that high concentrations of  $Pb^{2+}$  in an effluent will not impair the ability of the PHC to adsorb other metals.

#### 4. Modeling

Understanding the mechanism of metal ions interaction is essential to the control of the adsorption process. Several groups of workers have described the reaction order of sorption in metal-carbon systems using various kinetic models. One of the main goals of this study was, therefore, to

Table 7  
Some properties parameters of metals

Metal	Ionic radius $A^\circ$	Ionic mobility ( $cm^2 \cdot V^{-1} \cdot s^{-1}$ )	Hydration energy (kcal/ion-g)	Diffusion coefficient $\Delta \cdot 10^5\ cm^2 \cdot s^{-1}$ at 25°C
Cadmium	0.60	54.0	539	0.721
Nickel	0.74	54.1	511	0.720
Zinc	0.83	53.5	496	0.714
Lead	1.26	70.0	362	0.930

apply a model, which can describe and predict sorption kinetics for any value of the initial concentration. (1)

Traditionally, the kinetics of  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  on PHC may be described following the first-order rate expression originally given by Lagergren [27] which is a special case for the general Langmuir rate equation. It has been developed by several authors [2,3,11,28–30] for particle diffusion controlled sorption process:

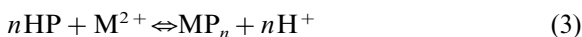
$$\text{Log} \frac{Q_e - Q_t}{Q_e} = -\frac{K_{ad} \cdot t}{2.3} \quad (1)$$

where  $Q_t$  and  $Q_e$  are the amounts of  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  adsorbed at time  $t$  and at equilibrium time, respectively, and expressed in  $\text{mmol} \cdot \text{g}^{-1}$ .  $K_{ad}$  is the rate constant of adsorption corresponding to particle size of the sorbent ( $\text{min}^{-1}$ ).

Since PHC contains functional groups, which can be involved in chemical bonding, PHC-metal ion reaction may be represented in two ways taking  $n$  as the general order of reaction:



and



where  $\text{P}^-$  and  $\text{HP}$  the active sites on the PHC surface. The rate expression for the sorption described by Eqs. (2) and (3) is:

$$\frac{d(\text{P})}{dt} = k(\text{P}_0 - \text{P}_t)^n \quad (4)$$

or

$$\frac{d(\text{HP})}{dt} = k(\text{HP}_0 - \text{HP}_t)^n \quad (5)$$

where  $\text{P}_t$  and  $\text{HP}_t$  are the number of active sites occupied on the PHC at time  $t$ ,  $\text{P}_0$  and  $\text{HP}_0$  are the number of equilibrium sites available on the PHC. Taking into account that in the range of time studied, the adsorption process rate ( $dq/dt$ ) is proportional to the difference ( $Q_{\max} - Q_t$ ) between the maximum concentration adsorbed at equilibrium and the concentration at time  $t$ , the following equation has been proposed as a kinetic

model where  $k$  ( $\text{mmol} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ ) is the rate constant and  $n$  represents the order of the process.

$$\frac{dq}{dt} = k(Q_{\max} - Q_t)^n \quad (6)$$

Differently, an alternative approach [31] of fitting the data with an empirical expression, noted as the hyperbolic equation, was applied:

$$Q = \frac{Q_{\max} \cdot B \cdot t}{1 + B \cdot t} \quad (7)$$

where  $Q$  represents the quantity of  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  adsorbed per unit mass of PHC for a time  $t$ .  $Q_{\max}$  is the maximum quantity of metal ion adsorbed per gram of adsorbent.  $B$  is a constant.

Using batch studies, many authors have shown the advantages of the kinetic equations described above over other classical equations in fitting the experimental data. Applicability of the desired equation is rather limited depending on many factors (nature of support, type of metals, operation conditions). Consequently, before it can be recommended, in an attempt to present the best equation representing our data sorption of divalent metals onto PHC, comparison of theoretical results with experimental data has been performed.

#### 4.1. Isotherm modeling

For the analysis of kinetics, equilibrium sorption of  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  on PHC was carried out at fixed temperature using various initial concentrations ( $0-1 \text{ mmol} \cdot \text{l}^{-1}$ ). The experimental data corresponding to the isotherms were plotted (Fig. 6) according to Freundlich and Langmuir equations, which can be represented in linear forms as follows:

$$\text{Langmuir model (I): } \frac{C_e}{Q_e} = \frac{1}{Q_0 \cdot b} + \frac{C_e}{Q_0} \quad (8)$$

$$\text{Langmuir model (II): } \frac{1}{Q_e} = \frac{1}{Q_0 \cdot b \cdot C_e} + \frac{1}{Q_0} \quad (9)$$

$$\begin{aligned} \text{Freundlich model : } & \text{Log } Q_e \\ & = \text{Log } k + n \text{ Log } C_e \end{aligned} \quad (10)$$

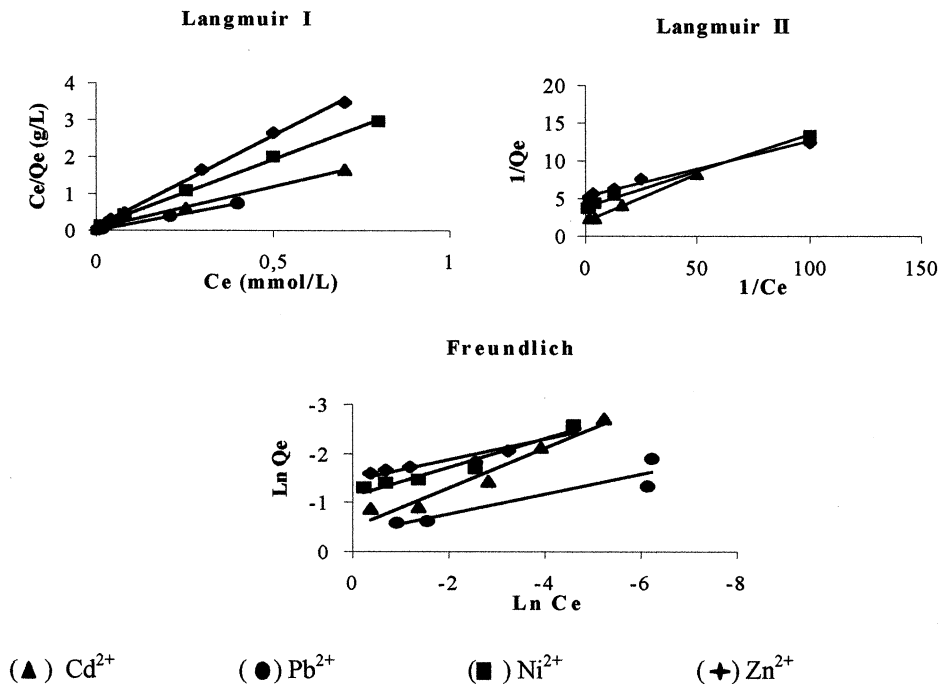


Fig. 6. Adsorption isotherm of Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup> and Cd<sup>2+</sup> in linear forms of Langmuir (I), Langmuir (II) and Freundlich models.

Table 8  
Adsorption isotherm constants of Langmuir and Freundlich models

Metal type	Langmuir model (I)			Langmuir model (II)			Freundlich model		
	$Q_0$	$b$	$R^2$	$Q_0$	$b$	$R^2$	$K$	$n$	$R^2$
Zn <sup>2+</sup>	0.20	42	0.999	0.19	71	0.987	0.23	0.2	0.914
Ni <sup>2+</sup>	0.28	24	0.999	0.26	41	0.978	0.32	0.3	0.940
Cd <sup>2+</sup>	0.45	24	0.999	0.47	17	0.985	0.60	0.5	0.951
Pb <sup>2+</sup>	0.55	180	0.999	0.87	89	0.976	0.70	0.2	0.875

where  $C_e$  is the equilibrium concentration ( $\text{mmol}\cdot\text{l}^{-1}$ ),  $Q_e$  is the amount adsorbed at equilibrium ( $\text{mmol}\cdot\text{g}^{-1}$ ) and  $Q_0$ ,  $b$ ,  $k$ ,  $n$  are Langmuir and Freundlich constants related to adsorption capacity and energy of adsorption which were calculated and represented in Table 8. As can be observed, experimental data were better fitted to the Langmuir equation ( $R^2 = 0.999$ ) than to the Freundlich equation and therefore, it is more suitable for the analysis of kinetics. Consequently,

the sorption process of metal ions on PHC follows the Langmuir isotherm model where the metal ion are taken up independently on a single type of binding site in such a way that the uptake of the first metal ion does not affect the sorption of the next ion. As a result,  $Q_0$  varied in the order  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$ . Budinova et al. [23] and Lopez et al. [31] reported a similar relationship when active carbon obtained from different raw materials were used as the adsorbent.

## 4.2. Kinetic modeling

The fitting of experimental data to Eqs. (1), (6) and (7) was tested by plotting  $\log(Q_e - Q_t)$  versus time  $t$ ,  $1/Q = f(1/t)$  and the variation of the ad-

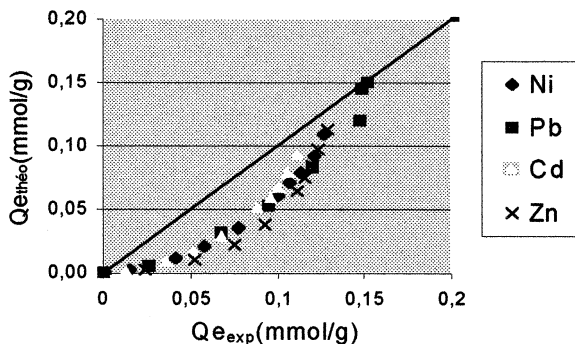


Fig. 7. Comparison of experimental adsorptive capacities  $Q_{e,exp}$  with calculated  $Q_{e,theo}$  values from the Lagergren equation.

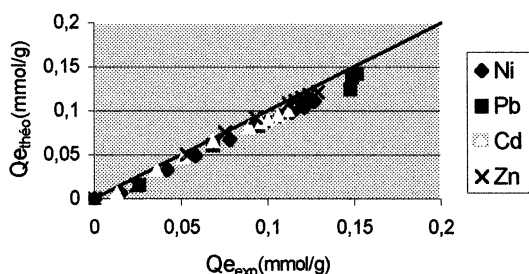


Fig. 8. Comparison of experimental adsorptive capacities  $Q_{e,exp}$  with calculated  $Q_{e,theo}$  values from the hyperbolic equation.

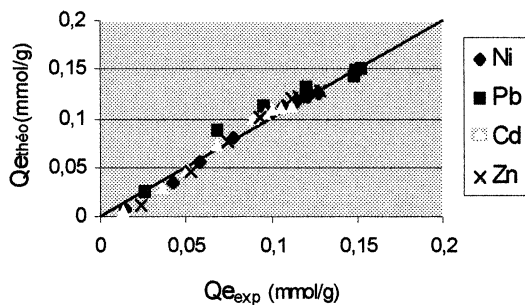


Fig. 9. Comparison of experimental adsorptive capacities  $Q_{e,exp}$  with calculated  $Q_{e,theo}$  values from the reaction rate equation.

Table 9

$k$  and  $n$  values according to the differential kinetic model

Metals	$k$ (mmol·mg <sup>-1</sup> ·min <sup>-1</sup> )	$n$
Cd	0.040	0.97
Ni	0.085	1.21
Zn	0.160	1.27
Pb	0.527	1.56

sorption process rate as a function of  $\log(Q_{max} - Q_t)$ , respectively. From the slope and intersection of the straight line obtained, the corresponding constant values were determined. Replacing these values in equations, theoretical values can be calculated and compared with the experimental data. The error indicator was the sum of the absolute values of the deviations between the experimental and the calculated sorption quantity of metal adsorbed. The goodness of fit was evaluated by the correlation coefficient  $R^2$  values obtained for each kinetic model.

Experimental  $Q_{e(experimental)}$  and theoretical results  $Q_{e(calculated)}$  were compared and represented as diagram of parity in Figs. 7–9. We can observe in the Fig. 7 that there is a large difference between experience and theory using the Lagergren equation. All experimental results were found under theoretical values. The equation does not describe adequately the kinetic and therefore, it should not be extrapolated to other conditions. Otherwise, as can be seen in Fig. 8, good correlation were obtained. The hyperbolic empirical equation gives a lower difference between experience and theory, the linear correlation coefficient obtained was  $R^2 = 0.986$ . It can provide a more appropriate kinetic relationship for the design of practical adsorption processes, but the values remain under-evaluate. On the other hand, the reaction rate equation is the more adequate because all the experimental points are very close to the theoretical points (Fig. 9), the linear correlation coefficient obtained was  $R^2 = 0.998$ . Consequently, we have accepted the last model as the best model describing our results. Therefore, the rate constants and the reaction orders issued from this model were calculated and were shown in Table 9. As can be observed, the values of  $k$  and

$n$  for  $Pb^{2+}$  is more important than for  $Cd^{2+}$ ,  $Ni^{2+}$  and  $Zn^{2+}$  allowing to confirm the high affinity and binding capacity of PHC for  $Pb^{2+}$ .

## 5. Conclusion

Peanut husks carbon is an effective adsorbent for the removal of  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$  and  $Ni^{2+}$  from aqueous solutions. It would be useful for the economic treatment of wastewater containing these heavy metals, as the adsorbent is derived from an agricultural waste by-product and its capacity is much superior to the commercial activated carbon. The adsorption is highly dependent on particle size distribution and on metal/PHC ratio. Various kinetic models were used to describe the adsorption process. The kinetic model according to the reaction rate equation was found to be the most in agreement with this system.

Since the removal of heavy metals by carbon can be a combination of factors such as adsorption, hydrogen bonding, precipitation and physical removal of insoluble metal complexes, further investigations to study the effect of the other operating conditions are necessary. At present, experiments are conducted in this way. All the PHC characteristics determined, together with the adsorption assays will play an important role in the future understanding of the adsorption processes of metals from aqueous solutions.

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