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Pb(II) and Cd(II) Removal from Aqueous Solutions Using Activated Carbon Developed from Coffee Residue Activated with Phosphoric Acid and Zinc Chloride

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ABSTRACT: Coffee residue, a low-cost agricultural byproduct, was tested as a precursor for the production of porous carbons in a chemical scheme using phosphoric acid and zinc chloride. The raw material was impregnated with increasing impregnation ratio (mass of $ZnCl_2$ or H_3PO_4/mass of coffee residue) from (0 to 100) % followed by pyrolysis at 600 °C for 1 h. The products were characterized by adsorption of N_2 at 77 K and proved to be highly microporous with high surface area. The impregnation ratio had a strong influence on the pore structure of these activated carbons, which could be easily controlled by simply varying the proportion of activating agents used in the activation. Thus, a low impregnation ratio led to essentially microporous activated carbons. At intermediate and high impregnation ratios, activated carbons with a wider pore size distribution (from micropores to mesopores) were obtained with high surface area. These low-cost adsorbents developed with $ZnCl_2$ and H_3PO_4 were used for the removal of lead(II) and cadmium(II), and they showed a substantial capability to adsorb lead(II) and cadmium(II) ions from aqueous solution. The kinetics of adsorption and extent of adsorption at equilibrium were dependent on the physical and chemical characteristics of the adsorbent, adsorbate, and experimental parameters. The effect of contact time and initial concentrations of adsorbate on the uptake of lead and cadmium was studied in batch experiments. The kinetic data were fitted to pseudofirst-order and pseudosecond-order models and follow closely the pseudosecond-order model. Equilibrium adsorption isotherms of Pb(II) and Cd(II) were analyzed by the Langmuir and Freundlich isotherm models. The Langmuir model gives a better fit than the Freundlich model.

INTRODUCTION

Nowadays heavy metals are among the most important pollutants in source and treated water and are becoming a severe public health problem. Industrial and municipal waste waters frequently contain metal ions. Industrial waste constitutes the major source of various kinds of metal pollution in natural water.[1−4] Recently, the application of sorption in environmental treatment has become a significant research area. Heavy metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity.[5,6] The heavy metal ions are stable and persistent environmental contaminants since they cannot be degraded and destroyed. These metal ions can be harmful to aquatic life, and water contaminated by toxic metal ions remains a serious problem for human health.

Lead is one of the most useful of all metals and has been used since antiquity because of its wide distribution and its easiness to be extracted and to work with. It is also the metal that has the most damaging effects on human health. Environmental contamination by lead probably dates back to the Bronze Age. It can enter the human body through the uptake of food (65 %), water (20 %), and air (15 %). Human activities, such as fuel combustion, industrial processes, and solid waste combustion contribute to the rise of lead concentrations in the environment. Lead can reach water and soil through the corrosion of pipelines in water transportation systems and through the corrosion of paints. It cannot be broken down but can be converted to other forms. The E.U. limit for lead in drinking water is 50 $\mu g \cdot L^{-1}$.[7]

The cadmium concentration in nonpolluted natural water is usually lower than 1 $\mu g \cdot L^{-1}$. The maximum acceptable cadmium concentration in drinking water in the E.U. is 5 $\mu g \cdot L^{-1}$. In the past, the main sources of cadmium were steel production, nonferrous metal production, refining, cement manufacture, cadmium plating, battery manufacture, ashes from oil, waste and combustion, and phosphate fertilizers. Nowadays, because of concerns about its environmental toxicity, the use of cadmium has decreased. About two-thirds of the cadmium in use today comes from nickel−cadmium batteries, the rest from pigments, metal plating, and the plastic industry.[7]

The presence of lead, cadmium, mercury, iron, nickel, and others metals has a potentially damaging effect on human physiology and other biological systems when the tolerance levels are exceeded. Many methods of treatment for industrial wastewater have been reported in the literature.[8] Among these methods are neutralization, precipitation, ion exchange, and adsorption. For low concentrations of metal ions in wastewater, the adsorption process is recommended for their removal. The process of adsorption implies the presence of an "adsorbent" solid that binds molecules by physical attractive forces, ion exchange, and chemical binding. It is advisible that the adsorbent is available in large quantities, easily regenerable, and cheap.[9]

Activated carbons (granular or powdered) are the most widely used adsorbents because of their excellent adsorption capability for inorganic pollutants.[10] The properties of activated carbons depend on the activation process and the nature of the source materials. Moreover, in both physical and chemical activation processes, knowledge of different variables is very important in

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Table 1. Elementary Analyses of Coffee Residue

characteristics	moisture (%)	ash ratio (%)	extractibles ratio (%)	lignin ratio (%)	cellulose ratio (%)	hemicelluloses ratio (%)
coffee residue	5.36	3.16	22.17	8.78	25.39	37.33

developing the porosity of the carbons.[11] The high adsorption capacities of activated carbons are related to properties such as surface area, pore volume, and porosity.[12] Particularly, the development of micropores and mesopores is of great importance because it allows the porous carbons to adsorb large amounts and various types of chemical compounds from gas or liquid streams.

In principle, the methods for preparing an activated carbon can be divided into two categories: physical activation and chemical activation. In physical activation, a raw material is first carbonized, and the carbonized material is secondarily activated by steam or carbon dioxide; i.e., there are two steps: carbonization step and activation step. In chemical activation, a raw material is impregnated with an activating reagent, and the impregnated material is heat-treated under an inert atmosphere. The carbonization step and the activation step simultaneously progress in chemical activation. This method occurs at lower temperature than that of the physical methods. Therefore, it improves the pore development in the carbon structure. The type of chemical agent is selected as a function of the characteristics of the desired activated carbon. Molina-Sabio and Rodriguez-Reinoso[13] reported that KOH produces only widening of the microporosity to more heterogeneous micropores, whereas $ZnCl_2$ develops both wide micropores and low mesopores and H_3PO_4 large mesopores and even macropores.

Chemical activation using $ZnCl_2$ and H_3PO_4 has been studied by several researchers[13−15] using different preparation conditions. These chemicals are used to dehydrate the starting material and to retard the formation of tars during the activation and the carbonization process.

In the present study, we have investigated the influence of both the porous texture and the chemical nature of a series of activated carbons prepared from coffee residue on the adsorption process of lead(II) and cadmium(II) from aqueous solutions at 298 K under static conditions. Kinetic models were used to identify the possible mechanisms of such adsorption processes. The Langmuir and Freundlich models were used to analyze the adsorption equilibrium.

■ EXPERIMENTAL METHODS

Biomass Raw Material. Coffee residue with a particle size in the range from (0.2 to 1) mm was used as a raw material for preparation of activated carbons. This precursor was collected in coffee houses and households. The elementary analyses of the initial material are shown in Table 1.

Preparation of Activated Carbons. *Impregnation with Phosphoric Acid and Zinc Chloride.* The coffee residue collected from coffee houses was first washed with distilled water to remove water-soluble impurities and surface adhered particles and then dried at 60 °C. Afterward, the granular particles of the coffee residue were impregnated with $ZnCl_2$ or H_3PO_4 solution. An amount of 200 g of dried precursor material was thoroughly mixed with $ZnCl_2$ or H_3PO_4 at $ZnCl_2$ or H_3PO_4/coffee residue mass ratios of (25, 50, 75, and 100) % in separate jars. Impregnation was carried out at 85 °C for 7 h to ensure the access of activating agents to the interior of the precursor, and then the temperature of the mixture was increased to the boiling point until complete dryness for 24 h.[15]

Thermal Activation by Pyrolysis in an Inert Atmosphere. The samples were carbonized separately for 1 h at 600 °C in a furnace heated from room temperature to 600 °C at 10 $°C \cdot min^{-1}$ under a nitrogen flow of 150 $mL \cdot min^{-1}$. The chars obtained were cooled under nitrogen (N_2) flow to room temperature, and the weight losses due to carbonization were determined. All the $ZnCl_2$ was extracted from the pores of the carbons by washing, with a solution of hydrochloric acid and then with distilled water. Concerning carbonized samples impregnated with H_3PO_4, the washing was carried out only with hot distilled water. The resultant activated carbons was dried and ground to particles having an average size of 63 μm.[15]

Characterization of the Activated Carbons. *Surface Area and Porous Structure.* The pore structure characteristics of the resulting carbon were determined by nitrogen adsorption at 77 K by a Gas Sorption Analyzer (Quantachrome NOVA WIN2-Version 9.0). Prior to gas adsorption measurements, the carbons were degassed at 200 °C in a vacuum for a period of at least 24 h. Nitrogen adsorption isotherms were measured over a relative pressure (p/p_o) range from approximately 0.005 to 0.985. The BET surface area was determined by means of the standard BET equation applied in the relative pressure range from 0.06 to 0.3. The total pore volume was calculated at a relative pressure of approximately 0.985, and at this relative pressure all pores were completely filled with nitrogen gas. The Dubinin−Radushkevich (D−R) equation represented below

$$\log V = \log V_{mic} - D\left(\log\left(\frac{P}{P_0}\right)\right)^2 \qquad (1)$$

was applied to calculate the micropore volume (V_{mic}). The mesopore volume (V_{mes}) was obtained by deducting the micropore volume from the total pore volume. The average pore diameters were estimated from the BET surface area and total pore volume ($D_p = 4V_{tot}/S_{BET}$) assuming an open-ended cylindrical pore model without pore networks.[16]

Thermogravimetric Analysis (TGA). Thermogravimetric experiments were carried out by a thermogravimetric analyzer (SETARAM TG-DTA 92) to determine the pyrolysis behavior of the coffee residue, $ZnCl_2$-impregnated coffee residue, and H_3PO_4-impregnated coffee residue. Three samples, coffee residue, $ZnCl_2$-impregnated coffee residue, and H_3PO_4-impregnated coffee residue, were measured over the temperature range of (0 to 900) °C at a heating rate of 10 $°C \cdot min^{-1}$ under flowing of nitrogen gas.

Boehm Titration. The Boehm titration method can be described as follows: 0.5 g of activated carbon was placed in a series of flasks which contained 50 mL of 0.05 N sodium bicarbonate, sodium carbonate, sodium hydroxide, and hydrochloric acid. The flasks were sealed and shaken for 24 h. After 24 h, the solutions were filtered, and then 10 mL of each solution was pipetted and was titrated with 0.05 N sodium hydroxide and/or hydrochloric acid, depending on the original solution used. The amount of acidic groups on the activated carbon is calculated under the assumption that NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na_2CO_3, carboxylic and lactonic; $NaHCO_3$, only carboxylic groups. The number of surface basic sites is calculated from the amount of HCl that reacted with the carbon. The reaction between the reagents and the acidic oxygenated functional groups on the surface is based on the difference in

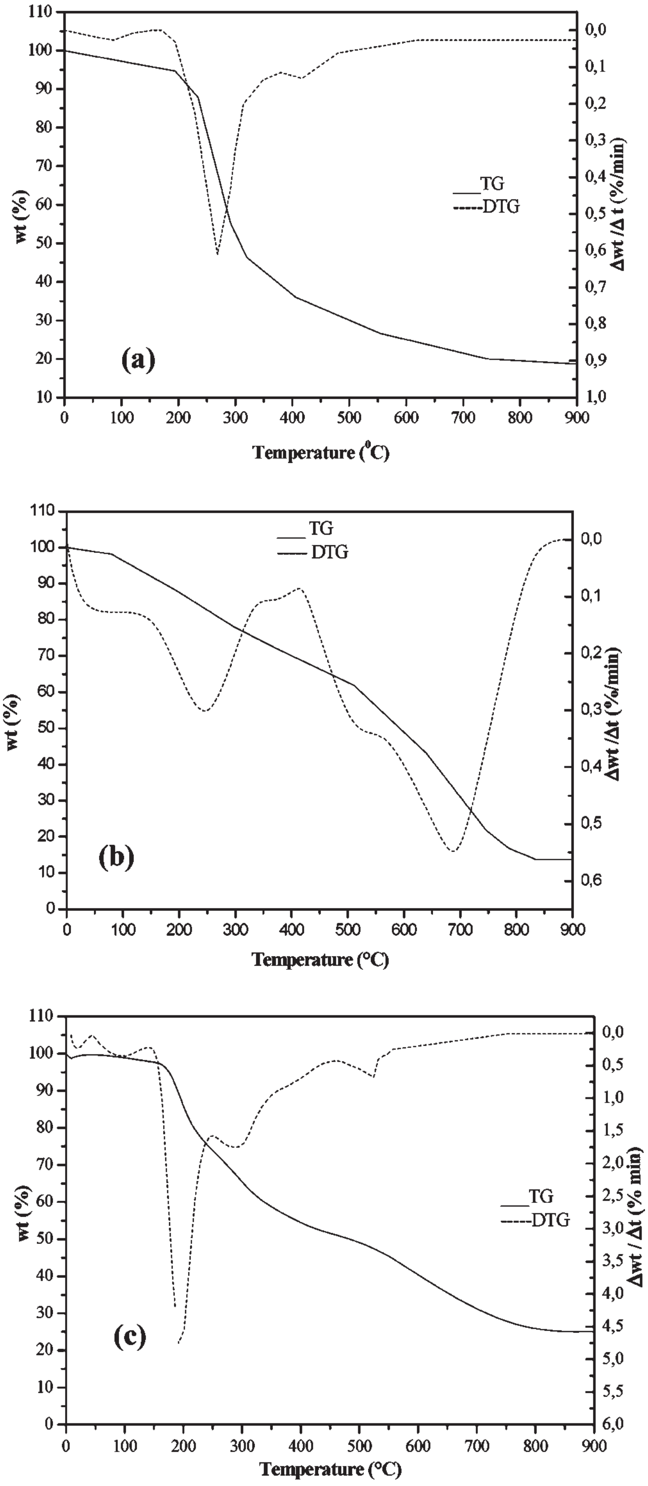

Figure 1. TG and DTG for (a) coffee residue, (b) H_3PO_4-impregnated coffee residue, and (c) $ZnCl_2$-impregnated coffee residue.

acid/base strength. The strength of acidic groups is as follow: carboxyl > lactone > phenol.[17]

Adsorbate and Analytical Measurements. All the compounds used to prepare reagent solutions are of analytical reagent grade. The stock solutions of Pb(II) and Cd(II) were prepared by dissolving the specific nitrate salts in distilled water. The initial ion concentrations ranged from (10 to 90) $\text{mg}\cdot\text{L}^{-1}$. The solution pH was adjusted to 5.8 by adding 0.1 M NaOH or 0.1 M HNO_3.

The concentration of the metal ions was determined using an atomic absorption spectrometer (AAS) (SCHIMADZU AA6500 atomic absorption spectrophotometer equipped with a Zeeman atomizer and a SSC-300). Absorption readings were taken at 283.3 nm for lead and 228.8 nm for cadmium. All samples were acidified with HNO_3 10 % (v/v) prior to the analysis. All the instrumental conditions are optimized for maximum sensitivity as indicated by the manufacturer.

Batch Sorption Procedure. Batch experiments of adsorption were performed in a batch reactor (3 L) placed in a temperature-controlled shaker (RCS LAUDA), at (25 ± 2) °C. A known weight of activated carbon was left in contact with 1000 mL of each solution [(10 to 90) $\text{mg}\cdot\text{L}^{-1}$] stirred at 200 rpm over 2 h. The initial pH value of the solution was adjusted with nitric acid (0.1 $\text{mol}\cdot\text{L}^{-1}$) or sodium hydroxide (0.1 $\text{mol}\cdot\text{L}^{-1}$). The pH value was chosen so that metallic species are present in their divalent form (5.8).[15] Small-volume liquid samples are withdrawn at different time intervals. Samples are filtered through glass-filter paper to remove adsorbent particles. The evolution of the adsorbed quantities of Pb(II) and Cd(II) ions was evaluated using the following equation

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

where q_e is the amount of ions adsorbed per mass unit of activated carbon; C_0 is the initial metal ion concentration ($\text{mg}\cdot\text{L}^{-1}$); C_e is the equilibrium metal ion concentration ($\text{mg}\cdot\text{L}^{-1}$); V is the volume of the aqueous solution (L); and m is the weight of adsorbent (g) used.

The adsorption percentage (% removal) of metal ions from aqueous solution is computed as follows

$$\text{removal } (\%) = 100\frac{(C_0 - C_e)}{C_0} \qquad (3)$$

Adsorption Isotherms. Both the Langmuir and Freundlich models were tested for equilibrium description. The Langmuir equation, based on a theoretical model, assumes monolayer adsorption over an energetically homogeneous adsorbent surface. It does not take into consideration interactions between adsorbed ions. It can be represented by the equation[18]

$$q_e = q_{\text{mon}}\frac{K_L C_e}{1 + K_L C_e} \qquad (4)$$

where C_e is the solute concentration ($\text{mg}\cdot\text{L}^{-1}$) at equilibrium; q_e is the amount of solute at equilibrium ($\text{mg}\cdot\text{g}^{-1}$); and q_{mon} and K_L are Langmuir constants related to adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$) and the energy of adsorption, respectively. The linear form of eq 4 can be written as

$$\frac{C_e}{q_e} = \frac{1}{q_{\text{mon}}K_L} + \frac{1}{q_{\text{mon}}}C_e \qquad (5)$$

The Freundlich equation is an empirical model based on heterogeneous adsorption over independent sites and is given by[19]

$$q_e = K_F C_e^{1/n} \qquad (6)$$

where K_F ($\text{mg}^{1-1/n}\cdot\text{L}^{1/n}\cdot\text{g}^{-1}$) and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. The

Table 2. Characteristics of Coffee Residue and Carbons Determined from N_2 Adsorption Isotherms at 77 K

activated carbons impregnated with $ZnCl_2$						activated carbons impregnated with H_3PO_4					
impregnation ratio (%)	S_{BET} ($m^2 \cdot g^{-1}$)	V_{mic} ($cm^3 \cdot g^{-1}$)	V_{mes} ($cm^3 \cdot g^{-1}$)	V_{tot} ($cm^3 \cdot g^{-1}$)	D_p (nm)	impregnation ratio (%)	S_{BET} ($m^2 \cdot g^{-1}$)	V_{mic} ($cm^3 \cdot g^{-1}$)	V_{mes} ($cm^3 \cdot g^{-1}$)	V_{tot} ($cm^3 \cdot g^{-1}$)	D_p (nm)
0	253	0.119	0.024	0.143	2.26	0	253	0.119	0.024	0.143	2.26
25	526	0.341	0.016	0.357	2.71	25	610	0.281	0.076	0.357	2.34
50	682	0.352	0.059	0.411	2.41	50	728	0.368	0.055	0.423	2.32
75	858	0.387	0.162	0.549	2.56	75	817	0.392	0.097	0.489	2.39
100	889	0.418	0.347	0.765	3.44	100	1003	0.423	0.195	0.618	2.46

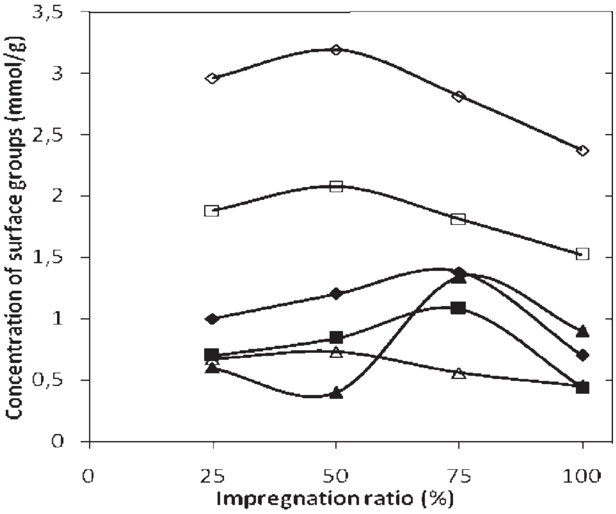

Figure 2. Boehm titration results of carbons prepared from coffee residue with different impregnation ratios and activating agents: -◆-, carboxylic groups-zinc chloride; -■-, carbonylic groups-zinc chloride; -▲-, phenolic groups-zinc chloride; -◇-, carboxylic groups-phosphoric acid; -□-, carbonylic groups-phosphoric acid; -△-, phenolic groups-phosphoric acid.

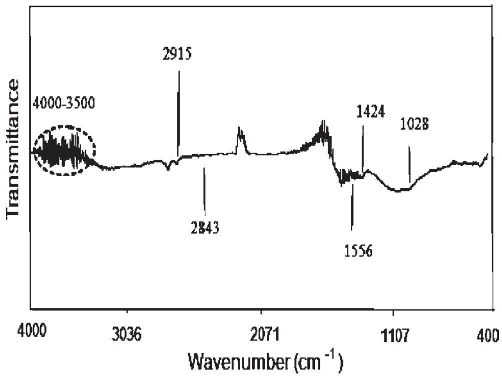

Figure 3. FTIR spectra of the prepared carbon impregnated with H_3PO_4 (50 % chemical ratio).

linearized form of eq 6 can be obtained by taking logarithms of both sides

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{7}$$

Adsorption Kinetics. The controlling mechanism of the metal adsorption process was investigated by fitting first- and second-order kinetic models to the experimental data. The linearized first-order kinetic model is given as[20]

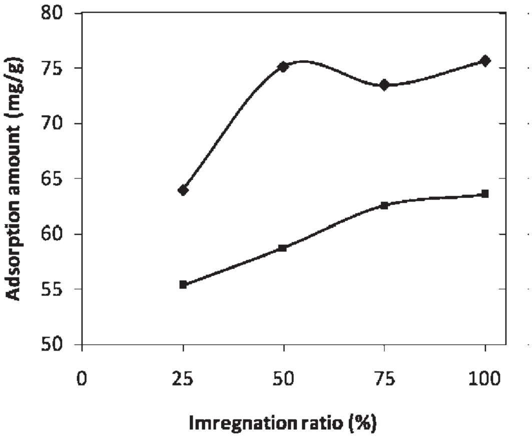

Figure 4. Effect of impregnation ratio on adsorption of lead(II) by activated carbons. Conditions: pH 5.8, agitation speed 200 rpm, agitation time 2 h, initial concentration of Pb(II) 90 $mg \cdot L^{-1}$ and 25 °C. -◆-, phosphoric acid; -■-, zinc chloride.

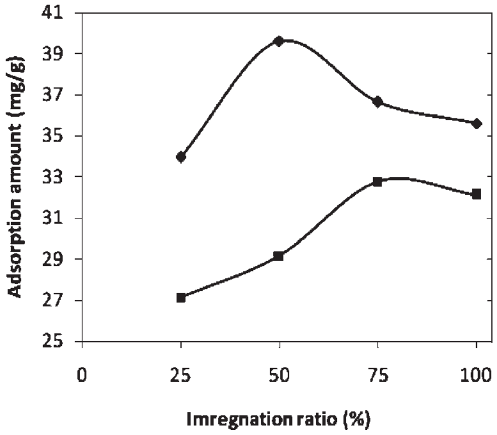

Figure 5. Effect of impregnation ratio on adsorption of cadmium(II) by activated carbons. Conditions: pH 5.8, agitation speed 200 rpm, agitation time 2 h, initial concentration of Cd(II) 90 $mg \cdot L^{-1}$ and 25 °C. -◆-, phosphoric acid; -■-, zinc chloride.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{8}$$

where q_t is the amount of adsorbate adsorbed at time t ($mg \cdot g^{-1}$); q_e is the adsorption capacity at equilibrium ($mg \cdot g^{-1}$); k_1 is the

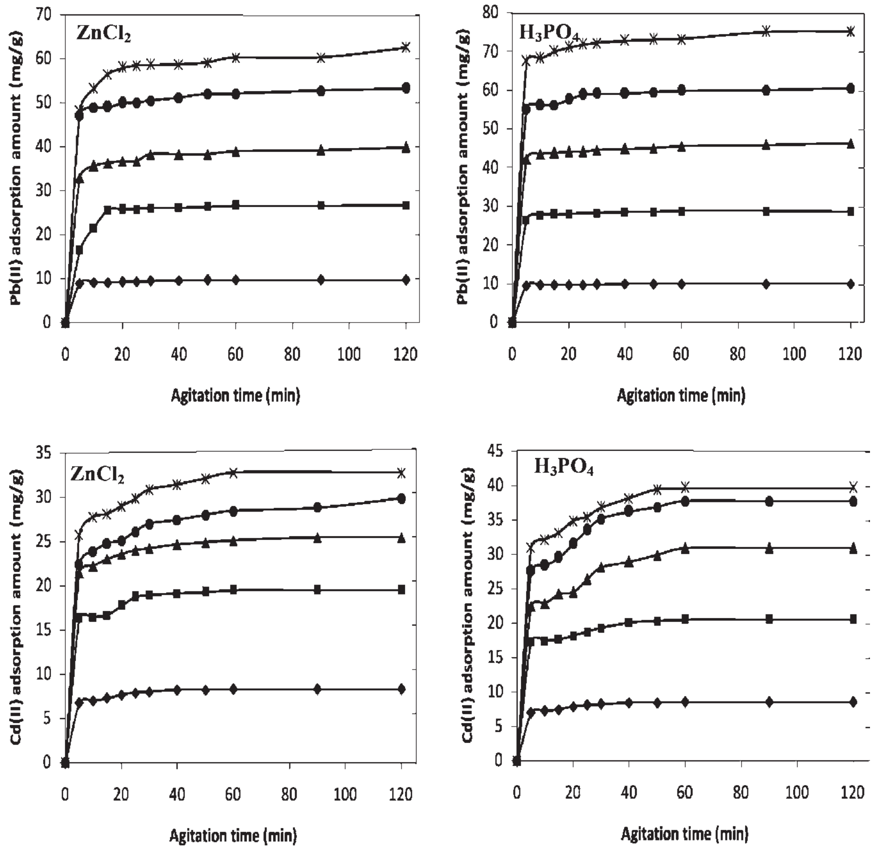

Figure 6. Effect of impregnation ratio on adsorption of Cd(II) and Pb(II) by activated carbons. Conditions: pH 5.8, agitation speed 200 rpm and 25 °C. -◆-. 10 $mg \cdot L^{-1}$; -■-, 30 $mg \cdot L^{-1}$; -▲-, 50 $mg \cdot L^{-1}$; -●-, 70 $mg \cdot L^{-1}$; -∗-, 90 $mg \cdot L^{-1}$.

Table 3. Pseudofirst-Order and Pseudosecond-Order Kinetic Parameters for Adsorption of Cd(II) and Pb(II) onto Activated Carbons

		concentration	q_e(exp)	pseudofirst-order			pseudosecond-order		
activated carbons	ion	($mg \cdot L^{-1}$)	($mg \cdot g^{-1}$)	k_1	q_e(cal) ($mg \cdot g^{-1}$)	R^2	k_2	q_e(cal) ($mg \cdot g^{-1}$)	R^2
impregnated with H_3PO_4 (50 % chemical ratio)	Pb(II)	10	9.90	0.074	0.99	0.961	0.204	10.00	1
		30	28.59	0.059	2.24	0.970	0.072	29.41	1
		50	46.17	0.028	4.12	0.973	0.019	47.62	0.999
		70	60.41	0.029	4.89	0.882	0.017	62.50	1
		90	75.15	0.040	10.79	0.887	0.009	76.92	0.999
	Cd(II)	10	8.45	0.087	3.00	0.967	0.075	8.62	0.999
		30	20.49	0.063	6.51	0.931	0.021	21.28	0.999
		50	30.88	0.048	13.25	0.963	0.007	32.26	0.998
		70	37.73	0.059	17.05	0.978	0.007	40.00	0.999
		90	39.61	0.076	19.45	0.872	0.009	41.67	0.999
impregnated with $ZnCl_2$(75 % chemical ratio)	Pb(II)	10	9.65	0.054	1.23	0.927	0.111	9.80	0.999
		30	26.69	0.048	4.39	0.822	0.019	27.78	0.999
		50	39.84	0.027	5.62	0.922	0.013	41.67	0.999
		70	53.21	0.028	6.31	0.984	0.012	55.55	0.999
		90	62.57	0.018	8.92	0.742	0.008	62.50	0.999
	Cd(II)	10	8.25	0.087	3.01	0.967	0.075	8.40	0.999
		30	19.49	0.065	5.42	0.944	0.028	20.00	0.999
		50	25.41	0.046	4.85	0.995	0.022	26.32	0.999
		70	29.88	0.024	7.12	0.951	0.009	30.30	0.999
		90	32.77	0.051	9.50	0.984	0.012	34.48	0.999

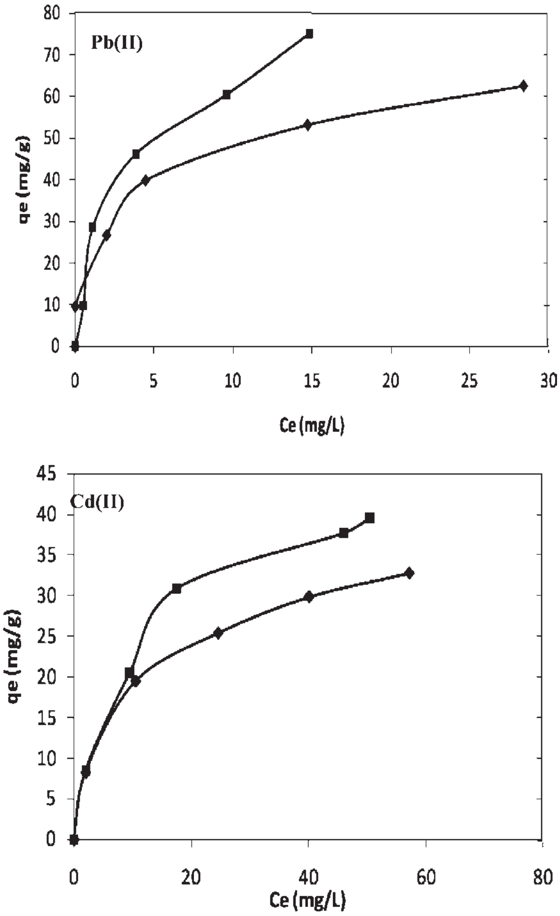

Figure 7. Adsorption isotherms of metal ions by activated carbons. Conditions: pH 5.8, agitation speed 200 rpm, agitation time 2 h and 25 °C. -◆-, zinc chloride; -■-, phosphoric acid.

pseudofirst-order rate constant (min^{-1}); and t is the contact time (min). The linearized second-order kinetic model is given as[21]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{9}$$

where k_2 is the equilibrium rate constant of pseudosecond-order adsorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$).

■ RESULTS AND DISCUSSION

Modifications in the Course of Pyrolysis under the Action of Phosphoric Acid and Zinc Chloride. During the pyrolysis of lignocellulosic materials, Rodriguez-Reinoso and Molina-Sabio[22] reported that three stages can be distinguished. These are: (a) loss of water in the (300 to 573) K range, (b) primary pyrolysis in the (573 to 773) K range with evolution of most gases and tars with formation of the basic structure of the char, and (c) consolidation of the char structure at (773 to 1123) K with a small weight loss. Despite the influence of the intrinsic chemical composition (relative content of the constituents: cellulose, hemicellulose, and lignin), the extrinsic factor of the chemical impregnation would be equally effective in directing the course of pyrolysis.

According to Figure 1, raw coffee residue exhibits only one prominent wave of weight loss [between (200 and 400) °C] with a maximum centered at 270 °C, followed by a slow weight loss with decreasing rate. A considerably different pattern is exhibited by the H_3PO_4-treated lignocellulosic material. A regular small weight loss covers the early stage between ambient and 400 °C, followed by another higher weight loss with increasing temperature from (400 to 700) °C. Beyond this temperature, the decomposing mass is still showing loss in weight at a slower rate up to 900 °C. Through this temperature range of (400 to 900) °C two DTG peaks appear with maxima at (525 and 700) °C. Thus, impregnation with H_3PO_4 brings about considerable effects on the course of pyrolysis of coffee residue (Figure 1): (i) it shifts degradation to considerably higher temperatures, (ii) it enhances the early dehydration stage combined with an evolution of low-boiling volatiles, (iii) it strongly retards the evolution of volatiles, where up to 600 °C only around 50 % weight is lost, whereas in the absence of H_3PO_4 complete degradation is finished before 600 °C, (iv) the principal degradation stage [(200 to 400) °C] is accompanied by a weight loss of only 17 % in the presence and 58 % in the absence of H_3PO_4, and (v) it promotes the carbon yield. These observations could be reasonably associated with the suggested mechanism, involving dissolution of some chemical components with bond cleavage, followed by recombination at other sites forming new polymeric structures that are thermally more resistant.[23]

Concerning the $ZnCl_2$/coffee residue mixture, two stages of thermal decomposition were observed in the thermal analysis (Figure 1). At the beginning, a release of moisture was recorded from ambient temperature to 125 °C. From (200 to 400) °C, a gradual weight loss appeared in the TG curve because of the pyrolysis of the residue in the mixture. As $ZnCl_2$ underwent a little weight loss at this stage, the existence of this agent in the mixture presents a significant effect on the decomposition of the residue because, in addition to its desiccating effect, it has a restriction action in the formation of tar, since the DTG peaks corresponding to the formation of tar and volatiles were practically absent. The DTG at 209 °C corresponds to the $ZnCl_2$ decomposition. From (400 to 600) °C, there was a weight loss contributing to the release of both $ZnCl_2$ and a few volatiles. Then, the carbon structure was readily formed.[24]

Development of Pore Structure. One of the primary parameters affecting the physicochemical properties of an activated carbon product manufactured by chemical activation is the degree of impregnation.[25−27] The pore structure characterization results obtained from nitrogen adsorption isotherms for samples prepared from coffee residue at 600 °C with different impregnation ratios are displayed in Table 2, where the impregnation ratio is defined as grams of H_3PO_4 or $ZnCl_2$ used per gram of dry precursor. It can be clearly seen that the BET surface area is influenced by the amount and the nature of impregnating agents. These results indicate that the BET surface areas of the activated carbons produced from coffee residue impregnated with two activating agents reached a maximum at an impregnation ratio of 100 %. The improvement of the BET surface areas is most likely due to the effect of the chemical agent which promotes condensation (polymerization) reactions. These reactions, which occur among the aromatic hydrocarbons and tar-forming compounds, result in the formation of large molecules (polycyclic aromatics) in the structure of activated products and increase the BET surface areas.

The chemical agent in the interior of the particles produces a dehydrating effect on the already transformed components (cellulose, hemicelluloses, lignin, etc.) during the heat treatment. It is very possible that cross-linking reactions are predominant in

Table 4. Langmuir and Freundlich Constants for Adsorption of Metals by Activated Carbons

		Langmuir			Freundlich		
activated carbons	ion	q_{mon} (mg·g^{-1})	K_L	R^2	K_F	n	R^2
impregnated with H_3PO_4 (50 % chemical ratio)	Pb(II)	89.28	0.288	0.978	19.41	1.86	0.903
	Cd(II)	46.95	0.100	0.995	6.64	2.11	0.966
impregnated with $ZnCl_2$ (75 % chemical ratio)	Pb(II)	63.29	0.396	0.997	27.49	4010	0.969
	Cd(II)	37.04	0.111	0.994	6.60	2.43	0.982

this step, with the subsequent reduction in the exit of volatile matter and tars leading to the high yield observed. Dehydration is favored because the chemical agent is as a liquid (melting point = 286 °C) at the temperature of the process, thus facilitating the bonding to the precursor being thermally degraded. It is also probable that the precursor transfers water to the reactant in the reacting mass to form a hydrated compound which loses water upon increasing temperature. The dehydration of the precursor produces a reduction in the dimensions of the particle, although such reduction is partially inhibited because the reactant remains inside during the thermal treatment, thus acting as a template for the creation of microporosity.

The surface areas of activated carbons developed from coffee residue impregnated with H_3PO_4 were much higher than that of carbons prepared with $ZnCl_2$. A similar trend is observed for the total pore volume calculated from the amount of the nitrogen adsorbed at relative pressure of $P/P_0 = 0.95$ (Table 2). The evolution of the micropore volume deduced from the Dubinin–Radushkevich equation (eq 1) and the mesopore volume with impregnation ratio is also shown in Table 2. It appears that the increase of the impregnation ratio increases the mesoporosity but slightly affects the development of the microporosity. The same results were reported by other authors.[28−30]

Effect of Impregnation Ratio on the Chemical Properties of Activated Carbons. Activated carbons contain different oxygen surface groups whose nature and amount depend on the starting material, the activating agent, and the activation treatment. The results obtained are presented in Figure 2. Carbons from both activating agents (H_3PO_4, $ZnCl_2$) attained a maximum amount of acidic surface groups at impregnation ratio values of (50 and 75) %, respectively.

When the impregnation ratios are greater than these optimal values, the concentrations of the three types of surface groups exhibit a slight decrease. At the same activation conditions, activated carbons prepared from H_3PO_4 possessed more acidic surface groups of different strength than activated carbons prepared from $ZnCl_2$ across the entire range of impregnation ratio investigated.

To qualitatively confirm the results obtained by the method of Boehm, we used FTIR analysis. In Figure 3, we presented the FTIR spectra for the activated carbon impregnated with H_3PO_4 (50 % optimal chemical ratio). It shows the following bands:

- 4000 cm^{-1} and 3500 cm^{-1} correspond to the OH groups of the phenol function;
- 2906 cm^{-1} and 2847 cm^{-1} correspond to stretching C−H groups of aliphatic, olefinic, and aromatic structures;
- 1556 cm^{-1} is attributed to stretching C=O of the carbonyl groups in quinine as well as γ-pyrone structure;
- 1424 cm^{-1} corresponds to stretching C−O or O−H deformation in carboxylic acids.

Table 5. Separation Factor Values for Heavy Metal Adsorption by Activated Carbons at Different Initial Concentrations

activated carbons	ion	concentration/ (mg·L^{-1})	r
impregnated with H_3PO_4 (50 % chemical ratio)	Pb(II)	10	0.258
		30	0.104
		50	0.065
		70	0.047
		90	0.037
	Cd(II)	10	0.500
		30	0.250
		50	0.167
		70	0.125
		90	0.100
impregnated with $ZnCl_2$(75 % chemical ratio)	Pb(II)	10	0.259
		30	0.104
		50	0.065
		70	0.047
		90	0.037
	Cd(II)	10	0.474
		30	0.231
		50	0.153
		70	0.114
		90	0.091

Concerning the activated carbon impregnated with $ZnCl_2$ (75 % optimal chemical ratio), Khenniche and Aissani[31] have prepared carbons from coffee residue impregnated by zinc chloride using the same conditions. These authors reported that all the carbons exhibit both acidic and basic surface functional groups.

In the effect of impregnation ratio on the formation of acidic surface groups, three sources are proposed to contribute to the formation of acidic surface groups on activated carbon developed from coffee residue activated with zinc chloride: (1) Hydrolysis of starting materials in acidic conditions. This source mainly leads to the formation of carboxylic groups of different strengths, and some of these groups begin to decompose at a temperature as low as 170 °C. (2) The reaction between activation agent and starting material or the hydrolysis products of the starting material. (3) The reaction between the starting material and air.[15,32]

The final activation temperature of 600 °C was used to prepare carbon samples with different values of impregnation ratio. At this temperature, source (1) is not the primary origin of acidic surface groups because of the decomposition of temperature-sensitive groups. At lower impregnation ratios, surface groups formed through source (2) are significant. With increasing impregnation ratio, surface groups contributed by source

Table 6. Comparison of Adsorption Capacity of Other Adsorbents

precursor	ion	activating agent	chemical ratio (%)	S_{BET} ($\mathrm{m}^2 \cdot \mathrm{g}^{-1}$)	q_{mon} ($\mathrm{mg} \cdot \mathrm{g}^{-1}$)	ref
Enteromorpha prolifera	Pb(II)	$ZnCl_2$	100	1398	147	37
hazelnut husks	Pb(II)	$ZnCl_2$	100	1092	13.05	38
charcoal	Pb(II)	H_3PO_4	50	-	1.17	39
			100	-	1.03	39
	Cd(II)		50	-	2.88	39
			100	-	4.18	39
nut shells	Cd(II)	H_3PO_4	100	1287	90.09	40
Tamarind wood	Pb(II)	$ZnCl_2$	100	1322	0.27	41
cattle-manure compost	Pb(II)	$ZnCl_2$	200	1752	6.15	42
apricot stone	Cd(II)	H_3PO_4	100	566	33.57	43
	Pb(II)		100	566	22.85	43
coffee residue	Cd(II)	$ZnCl_2$	75	858	37.04	present study
	Pb(II)		75	858	63.29	present study
	Cd(II)	H_3PO_4	50	1003	46.95	present study
	Pb(II)		50	1003	89.28	present study

(3) increase slowly, while surface groups coming from source (2) rapidly decline because of the prohibited diffusion of oxygen into the activation mixture.

Effect of Chemical Ratio on Adsorption Amount of Lead and Cadmium. The textural and chemical characteristics resulting from activation of coffee residue are important in the adsorption behavior and the adsorption capacity of activated carbons. The effect of impregnation ratio variation on the kinetics of lead and cadmium adsorption on activated carbons developed with H_3PO_4 and $ZnCl_2$ is reported in Figures 4 and 5. The adsorption amount of heav metals increases with an increase in impregnation ratio up to 75 % for activated carbons prepared with $ZnCl_2$ and 50 % for activated carbons treated with H_3PO_4. This may be attributed to the increase in adsorbent surface area, microporosity development, acidic functional groups, and availability of more adsorption sites resulting from an increase in impregnation ratio. All adsorption experiments in the following text are conducted with activated carbons prepared from coffee residue impregnated with 75 % ($ZnCl_2$) and 50 % (H_3PO_4) chemical ratios.

Adsorption Kinetics of Lead and Cadmium. The efficiency of the prepared carbons has been tested by subjecting them to the adsorption of lead and cadmium under the following conditions: pH = 5.8 at room temperature (25 °C), contact time of 2 h assured attainment of equilibrium for all the metal ions studied and in the presence of 1 g of carbon. The results obtained for the lead and cadmium adsorption tests are presented in Figure 6. It can be readily observed that sorption occurred at faster rates in the first 15 min for lead(II) ions and in 50 min for cadmium(II) ions. Results indicate that the time to reach equilibrium is slightly affected by the adsorbate initial concentration, but it is rather influenced by the nature of the metal ions in solution. For lower lead and cadmium ion concentrations, the ratio of surface active sites to total amount of metal ions is high, and thus all metal ions can more easily interact with the adsorbent and be removed from the solution. The adsorption efficiency was higher for lead ions than for cadmium ions. This behavior can be attributed to the fact that, at pH 5.8, the electrostatic repulsion between Cd(II) and the predominant positively charged surface of the adsorbent interfered with the adsorption process. The low but effective adsorption of the ions at pH 5.8 can be attributed either to isolated clusters of negatively charged sites distributed over the surface, where neighboring positively charged functional groups are not strong enough to cause repulsion to the ions, or to an ion-exchange mechanism with light metals comprising part of the husk composition.

The controlling mechanism of lead and cadmium adsorption was investigated by fitting first- and second-order models, given by eqs 8 and 9, respectively, to the experimental data for the adsorption dynamics. The results of the kinetic parameters for the two studied metal ions are presented in Table 3. The low correlation coefficient values obtained for the pseudofirst-order model indicate that sorption is not occurring exclusively onto one site per ion. On the basis of the correlation coefficients and the difference between q_e(exp) and q_e(cal) (Table 3), the adsorption for the lead and cadmium ions is best described by the pseudosecond-order model, which was developed based on the assumption that the rate-limiting step may be chemisorption promoted by either valency forces, through sharing of electrons between adsorbent and adsorbate, or covalent forces, through the exchange of electrons between the parties involved.[33] The values of the rate constant varied with initial concentration. Although consistency is expected for these values when a single controlling mechanism is assumed by the model, variations do occur for activated carbons and are usually attributed to the heterogeneous nature of the adsorbent surface.[34]

Adsorption Equilibrium. Adsorption isotherms are presented in Figure 7. The equilibrium adsorption data for all metal ions produced convex upward curves, which are indicative of strong adsorption.[35] The equilibrium capacity for metal ion sorption onto activated carbons impregnated with $ZnCl_2$ and H_3PO_4 increased upon increasing the initial metal ion concentration. The increasing initial metal ion concentration would increase the mass transfer driving force and therefore the rate at which metal ions pass from the solution to the surface of the activated carbon. Both the Langmuir and Freundlich models were evaluated for description of metal adsorption isotherms. Heavy metal adsorption from aqueous solutions by activated carbons was better described by the Langmuir model (see values of linear coefficients of determination (R^2) in Table 4) in comparison to the Freundlich model.

A characteristic of the Langmuir isotherm is the definition of a dimensionless factor r, called the separation factor

$$r = 1/(1 + K_L C_0) \qquad (10)$$

Adsorption is considered favorable when $r < 1$[36] which was the case in all tests in the present study (Table 5). Metal uptake capacity, represented by q_{mon} in the Langmuir equation, was higher for lead ions than for cadmium ions.

A comparison of the metal ion uptake capacities of activated carbons with other treated biomaterial-based adsorbents is presented in Table 6. A direct comparison is not possible because the differences in metal uptake capacities are due to a variety of parameters and conditions employed in each referenced work. Aside from the differences in experimental conditions, differences also exist in the properties of each adsorbent such as structure, functional groups, and surface area. However, qualitatively, it is evident that the metal uptake capacity of activated carbons prepared from coffee residue, in general, exceeds or is comparable to those for other adsorbents presented in Table 6. These results reinforce the feasibility of employing coffee residue as biosorbents for metal ion removal from aqueous solutions since they present good adsorption capacity in comparison to other low-cost sorbents.

■ CONCLUSION

Coffee residue has a high potential as a starting material for activated carbons showing good performance as an adsorbent for the treatment of waters containing heavy metals ions. The characteristics of the activated carbons obtained depend on the activation process and the nature of the chemical reagent. Chemical activation of the coffee residue with $ZnCl_2$ or H_3PO_4 produces activated carbons with a high specific surface area reaching about (889 and 1003) $m^2 \cdot g^{-1}$, respectively. It has been shown that the chemical ratio (mass of activating agent/mass of coffee residue) affects the physicochemical properties of the prepared carbons. Therefore, it is possible through a judicious choice of the activation ratio to obtain an activated carbon with desired characteristics.

A study of the feasibility of using activated carbon developed with coffee residue as treated biosorbent for the removal of lead(II) and cadmium(II) ions from aqueous solutions was successfully carried out. Activated carbons presented better adsorption performance for low concentrations of metal ions. After increasing the initial metal concentration from (10 to 90) $mg \cdot L^{-1}$, the adsorption efficiency (carbons activated with H_3PO_4) decreased to 83.5 % and 44 % for Pb(II) and Cd(II), respectively. The adsorption efficiency was higher for lead ions than for cadmium, at pH 5.8. The adsorption kinetics was best described by a pseudosecond-order model. Equilibrium was attained after 15 min of contact time for Pb(II) and 50 min for Cd(II). Adsorption isotherms were better described by the Langmuir model in comparison to the Freundlich model. The adsorption capacities were higher for Pb(II) and Cd(II) adsorption with the system H_3PO_4−coffee residue [(89.28, 46.95) $mg \cdot g^{-1}$] than for the system $ZnCl_2$−coffee residue [(63.29, 37.04) $mg \cdot g^{-1}$]. The activated carbons maximum sorption capacity (evaluated based on Langmuir fit) was higher than other treated residues such as sawdust, cocoa shell, etc.

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