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(RESEARCH ARTICLE)

Acid functionalization of activated carbon derived from coffee husks for the adsorption of lead in aqueous solution

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Abstract

This study is part of research into effective and less costly adsorbents for the removal of lead from aqueous solutions. Its objective is to functionalize activated carbon derived from coffee husks to improve its adsorption capacity. Activated carbon (AC) is obtained by chemical activation with a potassium hydroxide (KOH) solution. Functionalized carbon (AC-HNO_3) is obtained by impregnating AC with a 3N nitric acid solution followed by boiling at 120°C. The porosity of the activated carbons was studied by determining the iodine and methylene blue index. The surface chemistry of the activated carbons was evaluated by determining the pHzcp and surface functions. The performance of the carbons was evaluated for lead adsorption and studied as a function of contact time, carbon dose, solution pH and initial lead concentration. The elimination kinetics were monitored by atomic absorption spectrophotometry and then modelled according to pseudo-first and second order models. The iodine and methylene blue index were 482.3 and 18.56 mg/g and 336.1 and 35.8 mg/g, respectively, for CA and CA-HNO_3. The total acid and base site numbers are 2 and 2.5 meq/g and 6.21 and 1.51 meq/g, respectively, for CA and CA-HNO_3. The kinetic study of lead adsorption on these adsorbents follows the pseudo-second order model with a correlation coefficient of 0.99 and an equilibrium time of 75 min for both activated carbons. The quantities adsorbed at equilibrium are 6.64 and 7.35 mg/g for CA and CA-HNO_3, respectively.

Keywords: Acid Functionalization; Activated Carbon; Coffee Husks; Lead Adsorption

1. Introduction

The presence of trace metals in the environment is currently a concern in our societies [1]. Although these elements occur naturally in the environment [2], their high concentrations are linked to certain human activities such as agriculture and the metallurgical industry [3]. Their presence in the environment is problematic due to their bioaccumulation capacity and toxicity at low concentrations. They can cause diseases such as damage to the central nervous system, liver and kidneys, as well as cancer and embryonic malformations [4]. In addition, they can cause a decline in soil fertility and disrupt microbial fauna and aquatic biodiversity. The harmful effects of these pollutants on ecosystems and human health have been proven, making it necessary to detect and eliminate them [5] in order to protect humans and their environment. However, existing industrial treatment methods are costly [6]. Adsorption, a simple process to implement, is an alternative for the removal of trace metals in aqueous solution [7,8,9]. However, despite its excellent adsorption properties, commercial activated carbon remains inaccessible to developing countries due to its high cost [10]. In recent years, research has therefore focused on producing an adsorbent from local biomass

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with a view to making it more affordable. It is in this context that this work is being carried out, with the aim of functionalizing activated carbon obtained from coffee husks for the adsorption of lead in aqueous solutions. This modification, carried out by oxidation, allows the introduction of oxygenated functional groups [11], in particular carboxylic, phenolic and lactonic groups, which are responsible for the affinity of activated carbon with trace metal elements [12]. The surface functionalization of activated carbons, in terms of pollutant selectivity, offers many advantages that have been little exploited to date in the field of water treatment and therefore constitutes an avenue worth exploring.

2. Materials and Methods

2.1. Materials

2.1.1. Biological material

The biological material used consists of coffee husks, an agricultural by-product from the hulling of coffee cherries. This precursor was collected from a hulling facility located in the commune of Abobo, in the north of Abidjan, in Côte d'Ivoire.

2.1.2. Chemicals used

The products used for the preparation and characterization of activated carbons are listed in Table 1 below.

Table 1 List of products for the preparation and characterization of activated carbons

Name	**Chemical formula**	**Purity (%)**	**Manufacturer**
Potassium hydroxide	KOH	98	Fluka
Nitric acid	HNO_3	63	Panreac
Hydrochloric acid	HCl	36	Reidel de Haen
Sodium hydroxide	$NaOH$	99	Fluka
Sodium thiosulphate	$Na_2S_2O_3$	99	Panreac
Sodium carbonate	Na_2CO_3	≥ 99,5	Merck
Sodium hydrogen carbonate	$NaHCO_3$	≥ 99,5	Merck

2.2. Methods

2.2.1. Preparation of activated carbon

The preparation protocol adopted is that of [3] and can be summarised in three steps: pre-treatment of coffee husks, impregnation and carbonisation.

2.2.1.1. Pre-treatment of coffee husks

After receiving the coffee husks, they were washed with tap water and then rinsed with distilled water before being dried in a Memmert oven at 110°C for 24 hours. After drying, the material obtained was ground and then sieved to obtain particles ranging in size from 1 to 2 mm.

2.2.2. Impregnation of coffee husks

A 50 g sample of the pre-treated material was impregnated with 100 mL of a potassium hydroxide (KOH) solution with a concentration of 50 g/L. The impregnant was kept for 6 hours, then filtered and dried at 110°C for 24 hours until the impregnation liquid had completely evaporated.

Carbonization of pretreated husks

The dried coffee husks were carbonised at a temperature of 400°C for 3 hours in a Nabertherm muffle furnace. After cooling in a desiccator, the activated carbon obtained was washed with distilled water under agitation until the pH of the rinse water was close to neutral (between 6.5 and 7). It was dried in an oven and then stored in labelled food bags for later use.

2.2.3. functionalization of activated carbon

In a 250 mL Erlenmeyer flask, 10 g of previously prepared activated carbon (AC) was mixed with 100 mL of a 3N nitric acid solution. The mixture was placed on an Ovan hotplate set to 120°C with an isothermal plateau of 6 hours. After cooling, the functionalized activated carbon was rinsed with distilled water and then dried in an oven at 110°C for 24 hours. It was stored in food bags and labelled (AC-HNO_3) [13].

2.2.4. Characteristics of activated carbons (CA) and (CA-HNO_3)

Some characteristics related to porosity, namely the iodine index and methylene blue index of the two types of carbon, were determined in order to assess their adsorbent capacity [14]. In addition, the pH at the point of zero charge and the surface functional groups of these two adsorbents were determined in order to evaluate the effect of the functionalization on their surface chemistry.

2.2.5. Porosity study

- Iodine index

A suspension composed of 20 mL of a 0.02 N iodine solution and 0.2 g of activated carbon was stirred for 4 minutes and then filtered through filter paper. A volume of 10 mL of the filtrate was titrated with a 0.1 N sodium thiosulphate solution until it discolored. The procedure used in this study was that established by [15]. The amount of iodine adsorbed per gram of activated carbon, in milligrams, is given by the following equation

$$\text{Iodine index}(\frac{\text{mg}}{\text{g}}) = \frac{\left[C0 - \left(\frac{Cn \times Vn}{2VI2}\right)\right] \times MI2 \times Vads}{m}$$

With

- m (g): mass in grams of activated carbon used;
- V_{ads} (mL): volume of the iodine solution;
- C_0 (mol/L): concentration of the iodine solution;
- VI_2 (mL): volume of the iodine solution measured after adsorption;
- Vn (mL): volume of sodium thiosulphate added to achieve equilibrium;
- C_n (mol/L): concentration of the sodium thiosulphate solution;
- MI_2 (g/mol): molecular mass of iodine (254g/mol).

- Methylene blue index

Methylene blue adsorption tests were performed using the protocol described in [3]. A mass of 300 mg of activated carbon was placed in contact with 100 mL of a 1000 mg/L methylene blue solution and the mixture was stirred for 4 hours. After centrifugation, the suspension was analysed at a wavelength of 650 nm using an Aqualitic visual spectrophotometer to determine the residual concentration of methylene blue. The amount of methylene blue adsorbed is given by the formula below.

$$\text{Qm}(mg/g) = \frac{(Ci - Cf).V}{m}$$

With

- Ci: methylene blue initial concentration(mg/L);
- Cf: methylene blue final concentration(mg/L);
- V: volume of the methylene blue solution(mL);
- m: mass of activated carbon (mg)

2.2.6. Surface chemistry

2.2.6.1.1. pH at zero charge point

This method was inspired by the protocol in [16]. Volumes of 50 mL of a NaCl solution (0.01M) were placed in beakers, then the pH of the solution was adjusted from 2 to 12 by adding hydrochloric acid or 0.1N sodium hydroxide. A mass of

0.15 g of activated carbon was added to each solution, and the mixture was stirred for 48 hours. Each sample was then filtered, and the pH was measured again using a pH meter. The intersection points between the curve representing pHinitial = pHfinal and the curve representing pHfinal as a function of pHinitial represents the point of zero charge.

Surface functional groups

The protocol in [17] was used to determine the surface functional groups of the different activated carbons. The experiments to measure basic and acid functions were carried out as follows:

Measurement of basic functions

A mass of 0.5 g of activated carbon was placed in contact with 25 mL of a 0.1 N HCl solution, and the sample was kept under constant agitation for 48 hours using a stuart magnetic stirrer. After filtration, the excess HCl was titrated with a 0.05 N NaOH solution in the presence of phenolphthalein. The total basic functions were determined using the equation below.

$$Total\ basic\ (meq/g) = \frac{[[HCl] \times V(HCl)] - [NaOH] \times V(NaOH)]}{m}$$

With

- [HCl]: concentration of the hydrochloric acid solution (N);
- V(HCl): volume of the hydrochloric acid solution (mL);
- [NaOH]: concentration of the sodium hydroxide solution (N);
- V(NaOH): volume of the NaOH solution added at equivalence (mL);
- m(g): mass of activated carbon.

Dosage of acidic functions

- Carboxyl functions (GI)

A mass of 0.5 g of activated carbon was placed in contact with 25 mL of a 0.1 N $NaHCO_3$ solution, and the suspension was kept under constant agitation for 48 hours using a stuart magnetic stirrer. After filtration, the excess $NaHCO_3$ was titrated with a 0.05 N HCl solution in the presence of methyl orange as a colour indicator.

$$\mathrm{GI} = \frac{[\mathrm{NaHC03}] \times \mathrm{V(NaHCO3)} - [\mathrm{HCl} \times \mathrm{V(HCl)}]}{m}$$

With

- $V(NaHCO_3)$: volume of sodium hydrogen carbonate solution (mL)
- $[NaHCO_3]$: concentration of sodium hydrogen carbonate solution (N)
- V(HCl): volume of hydrochloric acid HCl solution added to equivalence (mL)
- [HCl]: concentration of the hydrochloric acid solution (N)
- m(g): mass of activated carbon.

- *Lactonic functions (GII)*

A mass of 0.5 g of activated carbon was placed in contact with 25 mL of a 0.1 N Na_2CO_3 solution, and the suspension was kept under constant agitation for 48 hours using a Stuart magnetic stirrer. After filtration, the excess Na_2CO_3 was titrated with a 0.05 N HCl solution in the presence of methyl orange.

$$\mathrm{GII} = \frac{[\mathrm{Na2CO3}] \times \mathrm{V(Na2CO3)} - [\mathrm{HCl}] \times \mathrm{V(HCl)}}{m} - \mathrm{GI}$$

Were

- $V(Na_2CO_3)$: volume of sodium carbonate solution (mL);
- $[Na_2CO_3]$: concentration of sodium carbonate solution (N);

- V(HCl): volume of sodium carbonate solution (mL);
- [HCl]: concentration of the sodium carbonate solution (N);
- m(g): mass of activated carbon

- *Phenolic functions (GIII)*

A mass of 0.5 g of activated carbon was placed in contact with 25 mL of a 0.1 N NaOH solution, and the suspension was kept under constant agitation for 48 hours using a Stuart magnetic stirrer. After filtration, the excess NaOH was titrated with a 0.05 N HCl solution in the presence of phenolphthalein as a colour indicator.

$$\text{GIII} = \frac{[NaOH] \times V(NaOH) - [HCl] \times V(HCl)}{m} - GII$$

With

- [HCl]: the concentration of the hydrochloric acid solution (N);
- V(HCl): the volume of hydrochloric acid solution poured at equivalence (mL);
- [NaOH]: the concentration of the sodium hydroxide solution (N);
- V(NaOH): the volume of the sodium hydroxide solution (mL);
- m(g): the mass of activated carbon used.

The number of sites of various acidic functions was calculated considering that $NaHCO_3$ neutralizes carboxyl groups, Na_2CO_3 neutralizes carboxyl and lactonic groups, and NaOH neutralizes carboxyl, lactonic and phenolic groups.

2.3. Lead adsorption

2.3.1. Influence of contact time

A mass of 0.2 g of each type of activated carbon (AC or AC-HNO_3) was placed in Erlenmeyer flasks containing 50 mL of a lead solution with a concentration of 10 mg/L. The mixture was stirred for a specific and varying period of time (ranging from 5 to 120 minutes). Samples were taken, centrifuged and then analysed using an atomic absorption spectrometer to determine the residual lead concentrations.

2.3.2. Influence of mass

Different masses of activated carbon (AC, AC-HNO_3) were placed in Erlenmeyer flasks, each containing 50 mL of a 10 mg/L lead solution. The mixture was stirred for a predetermined equilibrium time Te. After centrifugation, the samples were analysed by atomic absorption spectrometry to determine the residual lead concentrations.

2.3.3. Influence of the pH of the solution

To determine the influence of pH on lead adsorption, 100 mL reactors each containing 50 mL of a 10 mg/L lead solution were used. The pH of each solution was adjusted to the desired value (2 to 10) by adding 0.1N hydrochloric acid (HCl) solution or 0.1N aqueous sodium hydroxide (NaOH) solution. The optimal mass of carbon (CA, CA-HNO_3) previously obtained was introduced into each Erlenmeyer flask, and the mixture was stirred until equilibrium was reached. After centrifugation, the samples were analysed using an atomic absorption spectrophotometer to determine the residual lead concentrations.

2.3.4. Influence of initial concentration

The influence of initial concentration on adsorption was determined by varying the concentration of lead solutions from 10 to 40 mg/L. The pH of each solution was adjusted to the optimal value, then the optimal masses (mo) of the carbons (CA, CA-HNO_3) were introduced and stirred for the equilibrium time Te. After centrifugation, the samples were analysed by atomic absorption spectrometry to determine the residual lead concentrations.

2.3.5. Evaluation of adsorption capacity

This refers to the effectiveness of the adsorbent, which can be expressed in terms of the amount adsorbed (mg/g) or the adsorption rate (%). The amount adsorbed and the adsorption rate are given by the equations below, respectively.

$$Q_{a\,ds} = \frac{(C_0 - C_t)}{m_{CA}} * V$$

$$\text{rate} = 100 * \frac{C_0 - C_t}{C_0}$$

With

- Q_{ads}: adsorbed quantity in (mg/g)
- C_0: initial concentration of the solution in (mg/L)
- C_t: concentration of the solution at equilibrium (mg/L)
- V: volume in (mL) of the treated solution
- m(g): mass of activated carbon brought into contact with the solution.

2.3.6. Kinetic models of lead adsorption

Two models were used for the kinetic study of lead adsorption on our activated carbons. These are the model from [18] and the model from [19]. These mathematical models were chosen for their simplicity and their application in the field of adsorption of various compounds on different adsorbents. The characteristic rate constants of the pseudo-first-order and pseudo-second-order kinetic models were obtained from the equations below.

$$\log(\mathrm{q_e} - \mathrm{q_t}) = \log \mathrm{q_e} - \left(\frac{\mathrm{k_1}}{2{,}303}\right) t$$

$$\frac{t}{q_t} = \frac{1}{K_2 (q_e)^2} + \frac{1}{q_e}$$

Were

- q_e: quantities adsorbed at equilibrium
- q_t: quantity adsorbed at time t,
- K_1 (min^{-1}): rate constant for pseudo-first-order kinetics.
- K_2 ($g.mg^{-1}.min^{-1}$): rate constant for pseudo-second-order kinetics.

3. Results and Discussion

3.1. Characteristics of activated carbons

3.1.1. CA-HNO_3 and CA porosity

The iodine and methylene blue indices are two characteristics that provide information on micro- and mesopore porosity. The results for these two parameters are shown in Table 2.

Table 2 Iodine and methylene blue index of activated carbons

Adsorbent	Iodine index (mg/g)	BM index (mg/g)
CA	482,3	18,56
CA-HNO_3	336,1	35,8

The results recorded in Table 2 confirm the adsorbing power of the prepared activated carbons. However, functionalized activated carbon could be more effective for lead removal.

3.1.2. Surface chemistry

The study of the surface chemistry of activated carbons consisted of determining the pH of the zero charge point and the surface functional groups using the Bohem method. The results of these tests are shown in Table 3.

Table 3 Functional surface groups and Phi of activated carbons

Adsorbent	Phenol (Me/g)	Lactone (Me/g)	Carboxyl (Me/g)	Total Acid (me/g)	Total base (me/g)	pH zcp
CA	0	1,5	0,5	2	2,5	7,6
CA-HNO_3	0,98	1,82	3,41	6,21	1,51	2,8

The results of the characterisation tests show a modification in the surface chemistry of activated carbons. In fact, native carbon (CA) with a quasi-neutral surface and a total acidity of 2 meq/g for a total basicity of 2.5 meq/g, after functionalization, produces activated carbon (CA-HNO_3) with a predominantly acidic surface. This modification in surface chemistry is thought to be due to the partial oxidation of the CA surface. The strong oxidising agent nitric acid (HNO_3) causes the surface carbon atoms to lose electrons and become positively charged [20]. Moreover, the pH values at zero charge points, which are 7.6 and 2.8 for CA and CA-HNO_3 respectively, are consistent with the basic or acidic nature of the synthesised activated carbons. Indeed, according to [21], the more oxygenated groups the surface of carbonaceous materials contains, the more acidic these materials are. The low pH values at zero charge points of these functionalized activated carbons are due to oxidation and an increase in the acidic functional groups present on their surfaces [22]. The materials synthesised in this study have both basic and acidic functions that could promote the adsorption of anionic or cationic contaminants.

3.2. Lead adsorption kinetics

3.2.1. Effect of contact time

The equilibrium time is the time required for the adsorbent to fix the maximum amount of adsorbate. To determine this, the adsorption kinetics of lead on the two activated carbons, namely CA (native) and CA-HNO_3 (functionalized), were studied. The elimination kinetics are shown in Figure 1.

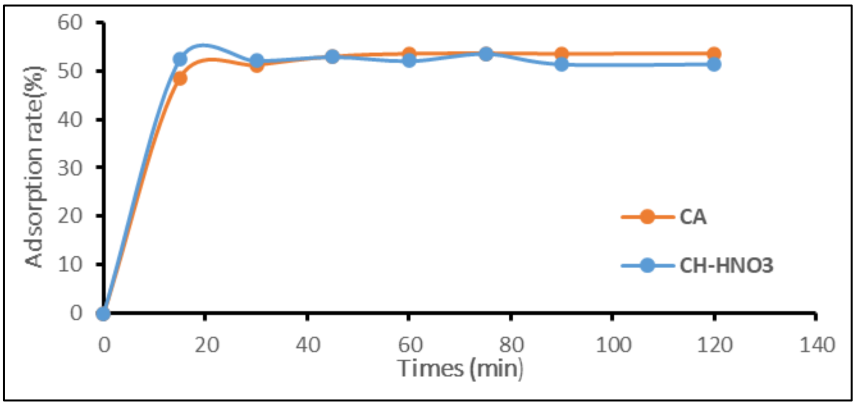

Figure 1 Effect of contact time on lead adsorption on CA and CA-HNO_3 (C_0=10 mg/L; m =0.05 g; pH = 6)

The shape of the curves shows that lead adsorption occurs in two stages. The first phase is rapid and covers the first 15 minutes of the process. It results in adsorption rates of 48.55% and 52.45% for untreated carbon (CA) and treated carbon (CA-HNO_3), respectively. The second phase, characterised by slow adsorption, begins after 15 minutes and ends at the end of the reaction. During this phase, the adsorption rates vary very slightly, reaching 51.35% and 53.48% for CA and CA-HNO_3 respectively. The rapid adsorption observed at the start of the reaction could be due to the availability of adsorption sites and the high concentration of Pb^{2+} ions. However, over time, the reduction in adsorption sites and ions in the liquid phase leads to the establishment of an equilibrium between the adsorbent and the solution, which manifests itself in the formation of a plateau. The work of [23] and [24] on the removal of copper and cadmium ions, respectively, reached similar conclusions. According to [23], the rapid adsorption observed at the start of the reaction is due to the existence of a very high affinity between the adsorbent and the adsorbate. Furthermore, [24] attributed it to the availability of active sites on the adsorbent, but also to an abundance of cadmium ions at the start. Finally, the last phase, which results in a plateau, is synonymous with the depletion of active sites available on the activated carbons. These results also reveal that functionalization has improved the adsorption properties of lead.

3.2.2. Effect of mass

Figure 2 shows the change in adsorption rate as a function of activated carbon mass.

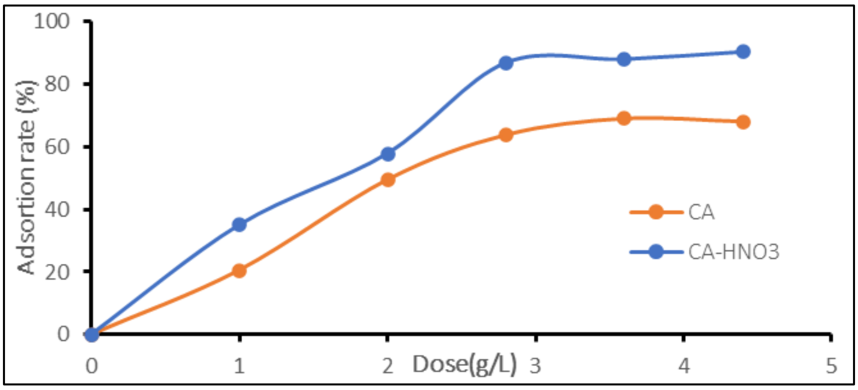

Figure 2 Effect of mass on lead adsorption (C_0 = 10 mg/L; pH = 6)

The curves in Figure 2 show an increase in the adsorption rate with increasing activated carbon mass. The adsorption rate increases from 20.53% to 67.93% for doses of 1 and 4.4 g/L of non-functionalized carbon (CA), respectively. For functionalized carbon (CA-HNO_3), this rate is significantly better, increasing from 35 to 90.23% for the same dose variations. However, above a dose of 2.8 g/L of CA and CA-HNO_3, the adsorption rate varies little despite the increase in carbon mass. The increase in the adsorption rate observed as a function of the mass of the carbons could be attributed to the availability of free adsorption sites, which increases with the amount of adsorbent. At low doses, Pb^{2+} ions easily access the adsorption sites of the carbons, hence the rapid increase in the amount adsorbed with the mass of the carbon. However, above a certain dose, the number of accessible free sites becomes stable. Thus, the addition of adsorbent increases the number of free sites, but these additional additions lead to the formation of agglomerations of coal particles, thereby reducing the adsorbent/adsorbate contact surface and consequently reducing the amount adsorbed. These results are consistent with those obtained by [25,26] in the removal of cadmium and lead by adsorption on activated carbon from apricot stones. According to these authors, the increase in the adsorption rate is due to an additional supply of adsorption sites following the increase in the mass of carbon. However, beyond a certain dose, the adsorption rate changes very slowly, giving way to a plateau that reflects a state of equilibrium between the activated carbon and the cadmium solution. This reduction in adsorption capacity could be attributed to the overlapping of adsorption sites, leading to a reduction in the total surface area [27].

3.2.3. Effect of solution pH

pH is a very important factor in the adsorption process. According to [28], as long as the surface charges of an adsorbent are modified by changes in the pH of the environment, pH remains one of the key parameters affecting the adsorption process of metal ions. In order to elucidate the effect of this factor on lead removal by activated carbon, adsorption tests were carried out at different pH levels. The results obtained are presented in Figure 3.

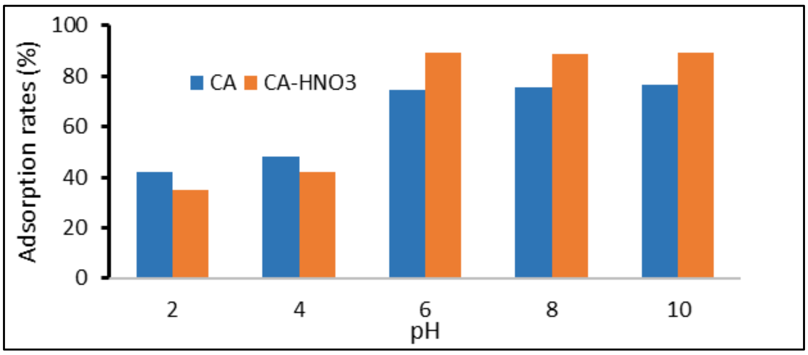

Figure 3 Effect of pH on lead adsorption (C_0 = 10 mg/L; dose = 2.8 g/L)

The test results show that elimination rates are low in acidic environments and increase with the pH of the solution.

Thus, the adsorption rates are 42% and 35% for CA and CA-HNO_3, respectively, at a pH of 2. These adsorption rates increase with the pH of the solution, reaching values of 74.7% and 89.1% for CA and CA-HNO_3, respectively, at a pH of 6. Above this pH, the rates vary slightly, reaching values of 76.8% and 89.5% for non-functionalized (CA) and functionalized (CA-HNO_3) carbon, respectively, at a pH of 10.

The low removal rate observed in an acidic environment is thought to be due to the existence of electrostatic repulsive forces generated not only by excessive protonation of the adsorption sites of the activated carbon, but also by the positive surface charges of the activated carbon at this pH value (pH≤ pHzcp) [29]. However, as the pH increases, the concentration of hydronium ions decreases, resulting in a reduction in repulsive forces and an increasingly negative surface of the activated carbon, which induces increasingly higher adsorbent/adsorbate attractive forces and therefore an increase in the adsorption rate [30]. The slight variation in adsorption observed above a pH of 6 indicates a state of equilibrium between the activated carbon and the solution. A pH of 6 represents the optimal pH for lead adsorption in an aqueous medium for both adsorbents. The results of this test show that the functionalization treatment improved the adsorption capacity of the treated activated carbon.

3.2.4. Effect of initial concentration

Aqueous solutions of Pb^{2+} metal ions with concentrations ranging from 10 to 40 mg/L were prepared in order to study their influence on the amount adsorbed, according to the experimental procedure described above. The results of this adsorption test are presented in Figure 4.

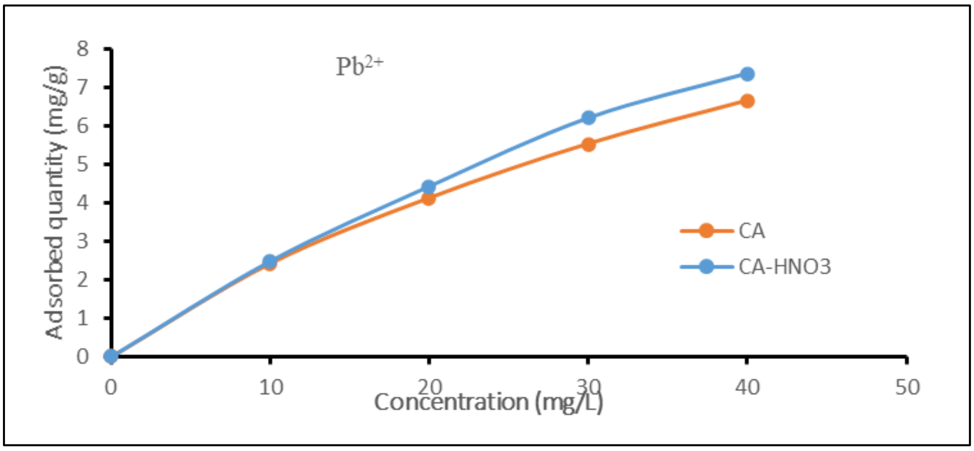

Figure 4 Effect of solution concentration on the amount of lead ions adsorbed

(Te = 75min; m = 0,05 g (2,8 g/L); pH = 6; Vsol = 50 mL)

Figure 4 shows the evolution of the adsorbed quantity as a function of the initial concentration. The results presented in Figure 4 indicate that an increase in the initial concentration of metal ions leads to an increase in the adsorbed quantity. The amounts of lead adsorbed increase with the initial concentration of the solution, reaching maximum values of 6.64 and 7.35 mg/g for untreated and treated coal, respectively, for concentrations ranging from 10 to 40 mg/L. The increase in the amount adsorbed could be explained by the ratio of the number of active sites on the surface of the coals to the number of ions present in the solution. At low concentrations, this ratio is high, leaving sites still unoccupied at equilibrium. According to [2], this improvement is due to the increase in the number of ions in the aqueous phase, which causes the adsorption equilibrium to shift towards the formation of more metal complexes in the solid phase. In fact, the transfer of the solute is all the more effective when the concentration of the solutions is high. Work on cadmium removal by adsorption, conducted by [4], has yielded comparable results. According to this author, this increase in the amount adsorbed with concentration could be explained by the existence of a strong concentration gradient of Cd^{2+} ions between the solution and the surface of the adsorbent, thus promoting the transfer of these metal ions to the surface of the adsorbent. The maximum amount adsorbed is obtained with functionalized activated carbon, thus demonstrating the beneficial effect of functionalization on lead adsorption. According to these results, regardless of the type of activated carbon, an increase in the initial concentration of metal ions leads to an increase in the amount adsorbed.

3.3. Kinetic modelling

The experimental and theoretical adsorbed quantities and the correlation coefficients of the pseudo-first and second order kinetic models of lead adsorption on the two activated carbons (AC and AC-HNO_3) are presented in Table 4.

Table 4 Parameters of the pseudo-first and second order kinetic models

			Pseudo-first-order kinetic model		**Pseudo-second-order kinetic model**	
ADSORBENT	C_0(mg/L)	$q_{e(exp)}$	q_{etheo}(mg/g)	R^2	q_{etheo}(mg/g)	R^2
CA	10	2,41	0,45	0,98	2,48	0,99
	20	4,11	0,62	0,94	4,19	0,99
	30	5,51	2,03	0,96	5,7	0,99
	40	6,64	2,93	0,98	6,95	0,99
CA-HNO_3	10	2,46	0,19	0,93	2,50	0,99
	20	4,40	0,71	0,96	4,50	0,99
	30	6,12	0,86	0,93	6,29	0,99
	40	7,34	1,12	0,95	7,5	0,99

These results show that the pseudo-second-order model gives correlation coefficients greater than 0.99 for both activated carbons. Furthermore, the theoretical adsorbed quantities determined using the pseudo-second-order model are very close to those obtained experimentally. The adsorption of lead on CA and CA-HNO_3 therefore follows the pseudo-second-order kinetic model.

Figure 5 shows the graphs of the kinetic models of lead adsorption on the activated carbons studied.

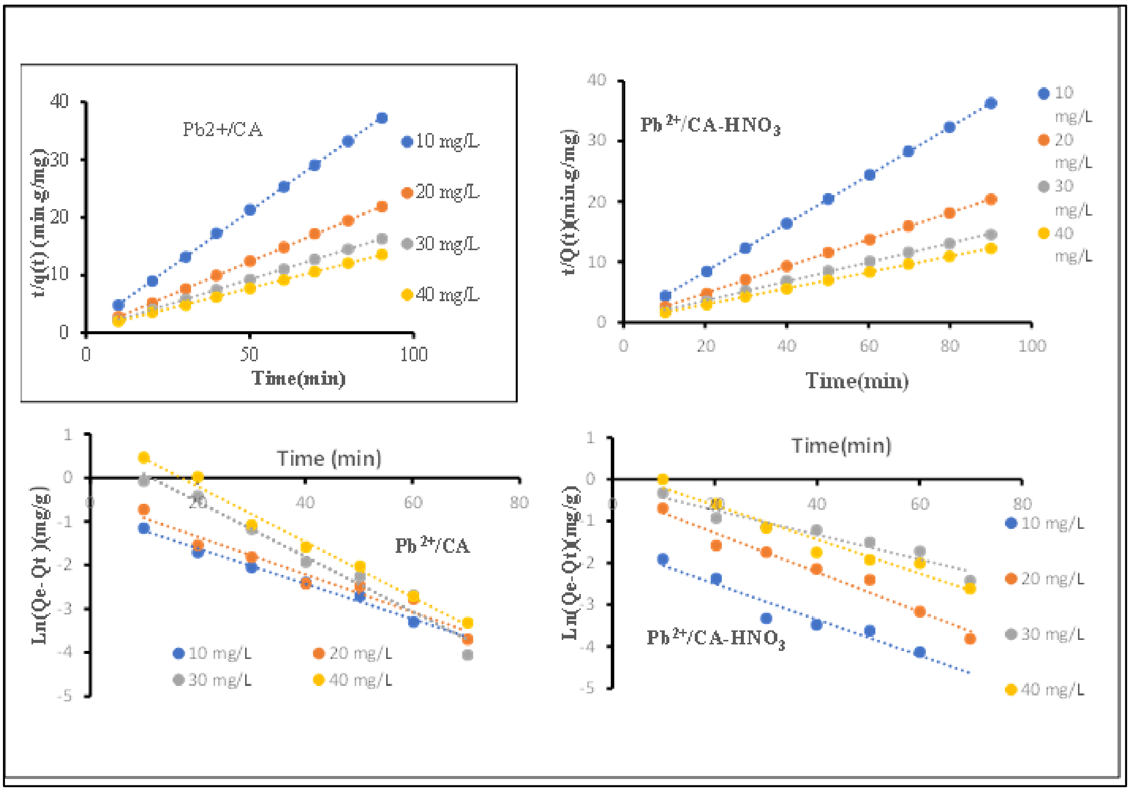

Figure 5 Kinetic models of lead adsorption on CA and CA-HNO_3

4. Conclusion

This study focused on the adsorption of lead on activated carbon made from coffee husks. The results of the characterisation tests revealed that functionalization led to an increase in acidic functions at the expense of basic functions. It also modified the porous structure, increasing mesoporousness. The study of the influence of parameters showed that the optimal contact time was 75 minutes with elimination rates of 48.55% and 52.45% for CA and CA-HNO_3, respectively. The increase in initial concentration led to an increase in the amount adsorbed to 6.64 and 7.35 mg/g for CA and CA-HNO_3, respectively, with an optimal dose of 2.8 g/L. The kinetic study showed that the adsorption process carried out in this study follows the pseudo-second-order model. At the end of this work, we conclude that the recovery of coffee husks into activated carbon is feasible. This activated carbon can undergo specific treatments such as functionalization to increase its affinity for the pollutant to be removed, in this case lead.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

Statement of Ethical statement

This study did not involve any human or animal subjects. All experiments were conducted in accordance with good laboratory practices and applicable ragulations regarding the the handling of chemical substances.

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