



Lead and cadmium removal from natural freshwater using mixed activated carbons from cashew and shea nut shells

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Abstract

Biomass wastes are potential low-cost and promising materials for removal of carcinogenic metals in contaminated waters. However, no information is available for cashew and shea nut shells that are abundantly grown in West Africa. We investigated lead and cadmium removal from aqueous solutions using activated carbons prepared from cashew and shea nut shells collected in Côte d'Ivoire, West Africa. The effects of contact time, initial concentration of cadmium(II) and lead(II), pH, and adsorbent mass were examined. The cashew and shea nut shells and their mixture were found to be good sorbents for cadmium and lead at an optimum mass dose of 12 g/L and pH 5.0 in synthetic solution. The adsorption rates varied between 94 and 99% for lead and between 86 and 94% for cadmium. The Langmuir model described isotherm of lead(II) ions adsorbed by shea nut shells, while lead adsorbed by cashew nut shells fitted the Freundlich model. The cadmium adsorption isotherms were described by Freundlich model. The Langmuir model best fitted lead and cadmium adsorptions by the mixture of the two activated carbons. Moreover, lead and cadmium adsorptions followed second-order kinetics. The cashew and shea nut shell activated carbons, and their mixture successfully removed cadmium and lead from natural freshwater.

Keywords Heavy metal · Adsorption isotherms · River water decontamination · Côte d'Ivoire

Introduction

Chemical pollutants are released into the environment as a result of many sources such as industrial, mining, and agricultural activities (Chakraborty et al. 2015; Kouassi et al. 2015; Toro et al. 2016). Among these chemicals, heavy metals are of great concern due to their toxicity, persistence, and non-biodegradability (Taiwo and Awomeso 2017; Fonseca et al.

2017). Hence, monitoring heavy metals pollution in the environment is very important.

Lead and cadmium are known to be toxic metals with no nutrient values. They are abundant almost everywhere in the nature. They incorporate into the food chain even at low concentrations in water systems, resulting in a wide variety of adverse effects in wildlife and humans (Zhang et al. 2017). Water birds exposure to sub-lethal dose of cadmium and lead

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induced behavioral changes and reproductive dysfunction, nephrotoxic effect, and renal and hematological toxicity (Marettov et al. 2015). Increased lead concentration has been found to coincide with a higher severity of histopathological alterations in freshwater fish gills (Fonseca et al. 2016). Lead and cadmium toxicity to humans and other mammals include renal failure, damages to reproduction parameters, neurological and digestive disorders, cardiovascular problems, skeletal weakness, mutations, and cancer (Marettov et al. 2015, Myong et al. 2014). In many parts of the world, especially in sub-Saharan Africa, most local populations do not have access to an improved source of drinking water (WHO 2006). Surface waters and groundwater are used without any treatment although the quality of these waters can be affected by metal lead and cadmium as a result of anthropogenic activities. For example, a recent study by Guy et al. (2018) found 31% of women's blood Pb concentrations exceeding the threshold level of 50 µg/L during pregnancy in Benin (West Africa). The authors identified water supply by drill pump and fishing by the household head among the potential sources of Pb exposure. Similarly, Ouattara et al. (2018) have revealed that 60% of water samples collected from the Bia River, Cote d'Ivoire (West Africa), during the flood season had Pb concentrations above the safety limit (10 µg/L) set by WHO for drinking water. Therefore, depollution of water contaminated by lead and cadmium through a cost-effective method is necessary both to protect the environment and for future use of these waters, and this was the focus of the present study.

Conventional methods including chemical precipitation, ion exchange, electrochemical treatment, membrane technologies, and sorption are used for removal of heavy metals from aqueous solution (Carolin et al. 2017; Ko et al. 2017; Liu et al. 2017; Visa 2016). These methods are very expensive. The adsorption technique with activated carbon appears to be well suited because of both its simple operation and metal removal efficacy (Sigdel et al. 2017). However, the high cost of activated carbon may increase the price of the water treatment. For these reasons, study of new and less expensive adsorbents has been the priority of many researchers. In this context, several studies have been conducted using agricultural by-products as adsorbents (Bouhamed et al. 2016; Elhafez et al. 2017). These studies have shown good adsorption capacities of low-cost biosorbents.

Shea and cashew nuts are very important in the social and economic context of many tropical regions due to their nutrition rates and commercial potentiality. However, the shells are burned or rejected in the environment after extraction of cashew and shea shell liquids, causing waste disposal problems. These low-cost waste products may be valorized through fabrication of activated carbon. A few studies on adsorption of metals by activated carbons of cashew and shea nuts have been carried out in Brazil and India (Coelho et al. 2014;

Kumar et al. 2011a, b, c; Jimoh et al. 2015). However, no information is available for cashew and shea nuts activated carbons from Africa. The objective of the present work was to investigate lead and cadmium removal by activated carbons and mixture activated carbons prepared from cashew and shea nut shells. To achieve this end, the influence of pH, contact time, adsorbent dose, and initial lead(II) and cadmium(II) concentrations was studied. In addition, a modeling of the kinetics and adsorption isotherms was carried out to better understand the mechanism of lead and cadmium adsorption on the carbon, and the capabilities of the cashew and shea nut shell activated carbons for removal of lead and cadmium were tested on typical freshwaters.

Materials and methods

Preparation of activated carbon

The cashew and shea nut shells were collected in Korhogo, northern Côte d'Ivoire, West Africa. The activated carbons were prepared following the procedure described by Gueu et al. (2007). The shells of the cashew nuts and the shea nuts were successively rinsed thoroughly with deionized water first to remove dust and soluble materials, dried at 105 °C for 24 h, impregnated with NaOH for 24 h, and dried at 105 °C for 12 h. Finally, cashew nut shells were carbonized at 500 °C for 4 h, and shea nut shells were carbonized at 450 °C for 2 h in an electric furnace (Advantech KL-280). The resulting materials were sieved to particle size of 47 µm. The obtained products were denoted as cashew activated carbon (CAC) and shea nut activated carbon (CAK). Three types of adsorbents, CAC, CAK, and ratio 1:1 mixture of CAC and CAK (CAC/CAK), were used for removing lead and cadmium ions from the synthetic wastewaters.

Chemicals and equipment

All chemicals and reagents were of analytical grade. Stock solution of 1000 mg/L of lead(II) and cadmium(II) was prepared from 1.6 g of lead nitrate $Pb(NO_3)_2$ (purity 99.5%, Carlo Erba) and 2.329 g of cadmium sulfate $CdSO_4 \cdot 3H_2O$ (purity 99%, Merck, Germany) using ultra-pure water. The desired concentrations of lead(II) and cadmium(II) varying from 10 to 50 mg/L were prepared by dilution of the stock solution by ultra-pure water.

The pH of each solution was adjusted to the required value with NaOH 0.1 M (purity 99%, Merck, Germany) or HCl 0.1 M (purity 37%, Scharlau, Spain). The concentrations of lead(II) and cadmium(II) ions in the solutions before and after equilibrium were determined using an air-acetylene flame atomic absorption spectrometer (AAS, SpectrAA100;

Varian, Tokyo, Japan). The pH values were measured using a pH meter HANNA HI.9828.

Batch adsorption studies

Batch experiments were carried out at room temperature (25 °C) to study the effect of pH, contact time, mass of activated carbons [CAC, CAK, and CAC and CAK (1:1)] and initial lead and cadmium concentrations.

The adsorption experiments were carried out by varying the pH, the contact time (0–90 min), the mass of the various activated carbons, and the initial concentrations of lead(II) and cadmium(II) (10–50 mg/L), respectively. Batch experiments were carried out in Erlenmeyer flasks. For all the tests, the solutions were agitated at 220 rpm and the suspensions were filtered through 47-mm pore size membranes (Millex Millipore, Merck, Damstadt, Germany) before analyses.

The effect of pH was investigated by setting the concentrations of lead(II) ion and cadmium(II) to 20 mg/L and varying the pH from 3 pH units to 8 at room temperature (25 °C).

The effect of adsorbent dose was carried out using 100 mL solutions of 20 mg/L of lead(II) and cadmium(II) ions for an adsorbent dose range of 2 to 20 g/L at room temperature (25 °C) and optimal pH of 5 pH units.

Each experiment was repeated three times, and the results reported correspond to the average values. The percent removal was calculated using the following equation:

$$\% \text{removal efficiencies} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of lead(II) and cadmium(II) ions (mg/L), respectively.

Adsorption kinetic experiments were carried out at 20 mg/L of lead(II) and cadmium(II) solutions, an equilibrium mass of 12 g/L for each activated carbon, and the optimum pH 5 at room temperature (25 °C). Samples were then removed at different time intervals (5, 10, 15, 20, 30, 40, and 60 min).

The amount q_t (mg/g) of metal ions adsorbed at time t was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_t (mg/L) is the lead(II) or cadmium(II) concentration in the solution after a contact time t (min), C_0 (mg/L) the initial concentration, V (L) the volume of the solution, and m (g) the mass of the adsorbent.

As for the adsorption isotherm experiments, lead(II) and cadmium(II) ion solutions at different concentrations (10, 20, 30, 40, 50 mg/L) at the optimal pH 5 were brought into contact with homogenized mass of activated carbons for the equilibrium time at 25 °C.

The quantity of lead(II) and cadmium(II) adsorbed at equilibrium, q_e (mg/g), was calculated following Eq. (3):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where q_e is the amount of lead(II) or cadmium(II) ions adsorbed at equilibrium (mg/g), V the volume of the solution (L), C_0 the initial concentration (mg/L), C_e the concentration at equilibrium (mg/L), and m the mass of the adsorbent (g).

Removal of lead and cadmium from natural freshwater

The capabilities of the cashew and shea nut shell activated carbons for removal of Pb and Cd from freshwaters were tested by performing batch experiments on typical surface waters collected from the Cavally River, Côte d'Ivoire. These waters were subjected to artisanal and industrial gold mining wastewater discharges. The total Pb and Cd concentrations were below the detection limits of 0.006 µg/L and 0.002 µg/L, respectively. Different Pb and Cd standard solutions were spiked and left react with different mass of activated carbons for 2 h (Sayed and Burham 2018). The pH was adjusted to 5 and kept constant. Experiments were carried out in triplicates, and the precision were less than 10%.

Theories

Modeling of adsorption kinetic

Pseudo-first-order (Lagergren et al. 1898) and pseudo-second-order (Ho and McKay 1999) were used to investigate the metals lead and cadmium adsorption kinetics on activated carbons.

The linear form of the pseudo-first-order is given by the following equation:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 \times t \quad (4)$$

where q_e and q_t (mg/g) are the amounts of the metal ions adsorbed at equilibrium and at time t (min), respectively, and k_1 (/min) the rate constant for the pseudo-first-order rate.

The kinetics of the pseudo-second-order model was described by using the equation:

$$\frac{1}{q_t} = \frac{1}{k_2 \times q_e^2} \times \frac{1}{t} + \frac{1}{q_e} \quad (5)$$

where k_2 (g/mg/min) is the rate constant for the pseudo-second-order rate equation.

Adsorption isotherm models

Langmuir and Freundlich adsorption models were used to describe the experimental data of adsorption isotherms.

Langmuir adsorption isotherm The model developed by Langmuir (1906) is represented by the linear equation:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m \times b} \times \frac{1}{C_e} \quad (6)$$

where C_e is the equilibrium concentration (mg/L), Q_e is the amount of adsorbate adsorbed per unit mass of the adsorbent at equilibrium (mg/g), b is the Langmuir adsorption constant (L/mg), and Q_m is the maximum amount per unit mass of adsorbent (mg/g).

The Langmuir equilibrium parameter (R_L) can be used to predict whether an adsorption system is “favorable” or “unfavorable.” The expression of R_L is as follows:

$$R_L = \frac{1}{1 + b \times C_0} \quad (7)$$

where C_0 is the highest initial solute concentration. The value of R_L indicates the type of the adsorption to be either unfavorable ($R_L > 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

Freundlich adsorption isotherm The general form of the Freundlich equation is given by Eq. (8):

$$Q_e = K_f \times C_e^{1/n} \quad (8)$$

where Q_e is the quantity of solute adsorbed at equilibrium (mg/g), C_e is the concentration at equilibrium (mg/L), and K_f and n are the empirical constants.

The linear form is given by Eq. (9):

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (9)$$

Results and discussions

Characterization of activated carbon

The nature and quantities of functional groups of activated carbons are shown in Table 1. There was some consistency between the pH values and the proportions of acid and basic functions. The two carbons contained higher total acid surface than total basic surface and presented low pH values. Both the activated carbons CAK and CAC showed an important surface area. However, the specific surface area of CAK (768 m²/g) was much greater than that of CAC (512 m²/g) indicating

Table 1 Physical and chemical characteristics of activated carbons

Activated charcoal		CAK	CAC
Physicals	Q_m (mmol/g)	6.00	4.11
	R^2	0.98	0.97
	SEBT (m ² /g)	768	512
Chemicals (Boehm, pH)	Acidic (mmol/g)		
	Carboxylic	0.30	0.20
	Lactone	1.12	1.04
	Phenolic	0.42	0.20
	Total acid surface	1.84	1.44
	Total basic surface	0.32	0.35
Structure	Surface pH	6.80	6.42
	Ash rate (%)	7.72	4.25
	Aspect	Powder	

higher adsorption capacity. Moreover, the high values of S_{BET} of CAK and CAC carbons indicated that KOH is effective in developing pores in CAK and CAC carbons.

Surface properties of the CAK and CAC activated carbons were compared with data from the literature (Table 2). The cashew nut shell BET surface area obtained in this study differed from 395 and 984 m²/g found by Kumar et al. (2011c, 2012), respectively. These differences could be explained by the geographic locations and the procedures used to prepare the activated carbons, as well as the biological characteristics of the cashew shells. The specific surface values of CAK and CAC were lower than those of Matured tea leaf (Goswami and Phukan 2017) and coconut shell (Song et al. 2014), and higher than those from Macore fruit (Aboua et al. 2015) and palm oil mill effluent (Adebisi et al. 2017).

Adsorption parameters

Influence of pH on adsorption efficiency

The pH of the aqueous solution is an important variable affecting adsorption of metals on adsorbents. Figure 1 shows that adsorption efficiencies of the lead(II) and

Table 2 Comparison of BET surface area (S_{BET}) with literature data

Adsorbents	S_{BET} (m ² /g)	Reference
Matured tea leaf (MTL)	1313	Goswami and Phukan (2017)
Macore fruit	229.5	Aboua et al. (2015)
Palm oil mill effluent	59.19	Adebisi et al. (2017)
Coconut shell	1135	Song et al. (2014)
Cashew nut shell	395.0	Kumar et al. (2011b)
Cashew nut shell	984.0	Kumar et al. (2012)
Shea-nut shell	768	This work
Cashew nut shell	512	This work

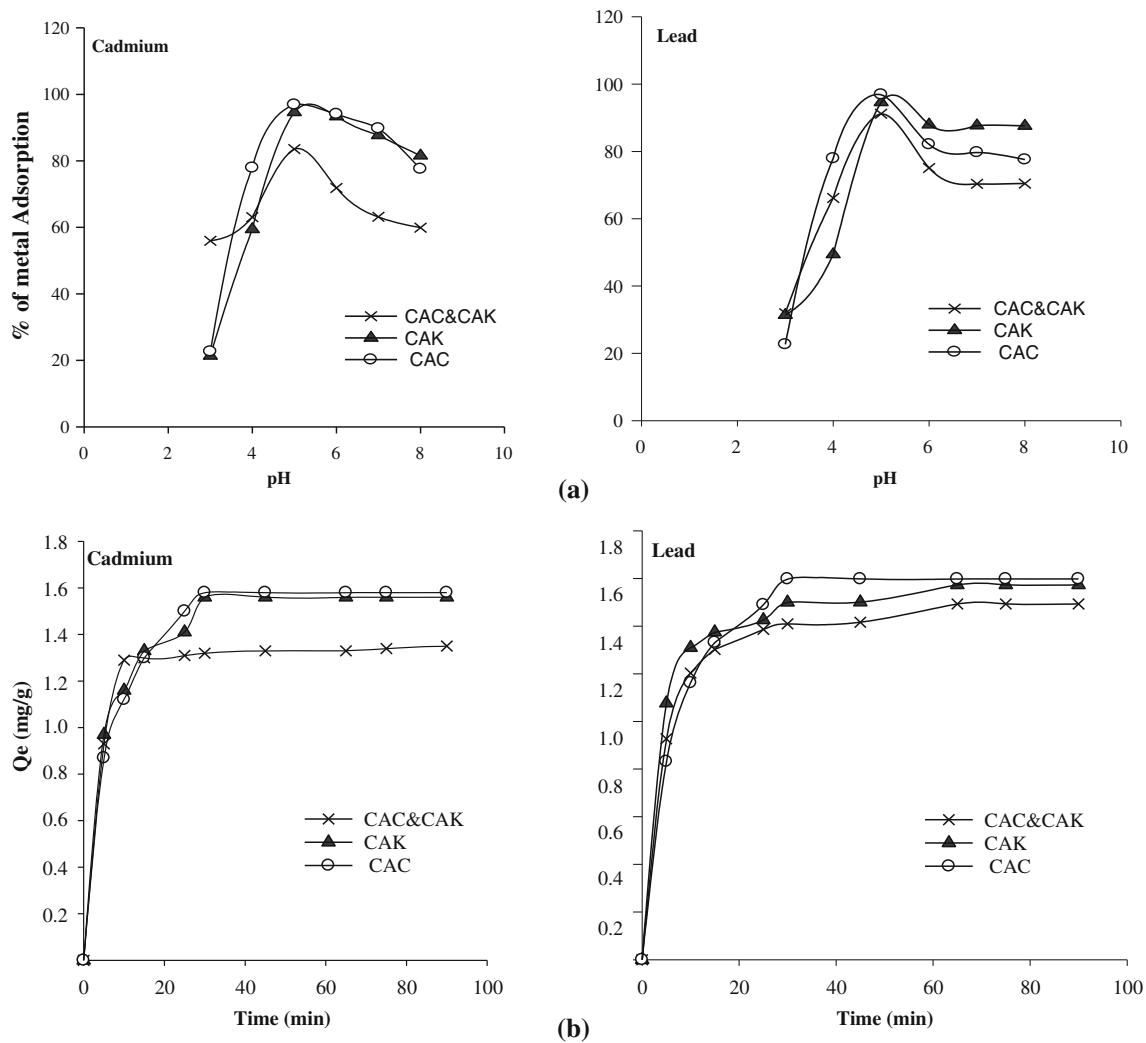


Fig. 1 Kinetics of cadmium and lead adsorption. **(a)** Effect of pH on removal rate and **(b)** effect of contact time on adsorption capacity (mg/g) of cashew nut shell (CAC) and shea nut shell (CAK) activated carbons, and the mixture CAC and CAK (1:1)

cadmium(II) ions increased with increasing pH of the medium. The optimum pH value for lead and cadmium removal appeared to be about 5.0. At low pH (<5), the percentage removal of lead and cadmium in aqueous solution was lowest due to competition between the excess of hydrogen ions and the positively charged metal ions toward the same active sites of the solid surface. At higher pH, the CAK, CAC, and CAC and CAK surfaces are more negatively charged thereby supporting more Cd(II) and Pb(II) biosorption due to electrostatic forces of attraction. However, at pH > 5, the biosorption capacity decreased with increasing pH. This result could be explained by the formation of anionic hydroxide complexes which decreases free Cd(II) and Pb(II) ion concentrations (Cheraghi et al. 2015). Our results suggest that pH < 5 are not favorable for metal lead and cadmium elimination by CAK, CAC, and mixed CAK and CAC carbons, while pH = 5 is appropriate to remove lead and cadmium in

aqueous solution by low-cost adsorbents. Similarly, Kumar et al. (2012) and Coelho et al. (2014) found optimum pH value of 5 for lead and cadmium removal by cashew nut shell activated carbons from India and Brazil, respectively.

Effect of contact time on adsorption efficiency

Contact time is unavoidably a basic parameter for transference phenomena, such as adsorption. The results of contact time influence on metals Pb and Cd removals by the cashew shell and shea shell are shown in Fig. 1. The adsorption increased sharply over the first 20 min and reached its optimum at 30 min, 60 min, and 65 min for CAC, CAK, and the mixture CAC and CAK, respectively. At equilibrium, the amounts of Cd(II) and Pb(II) biosorbed reflect the maximum biosorption capacity of CAC, CAK, and CAC and CAK under the operating conditions.

Effect of adsorbent mass and initial concentration on adsorption efficiency

Figure 2 shows the influence of adsorbents mass [CAC, CAK, and CAC and CAK (1:1)] and initial concentration on the lead and cadmium adsorption. The percentage removal of Pb and Cd increased with increasing the adsorbent mass because the higher mass, the more adsorbent sites. The maximum adsorption percentages of Pb and Cd were obtained with an adsorbent mass of 0.3 g (equivalent to a dose of 12 g/L). Coelho et al. (2014) found a similar adsorbent dose for activated carbons prepared from the cashew nut shell *Anacardium occidentale* L. from Brazil. After the equilibrium mass dose, the adsorption percentages remained constant. Therefore, an adsorbent dose of 12 g/L was sufficient to reach the maximum adsorption efficiencies of lead and cadmium (95–99% for CAC and CAK, and 81–86% for mixed CAC and CAK) in the synthetic solution.

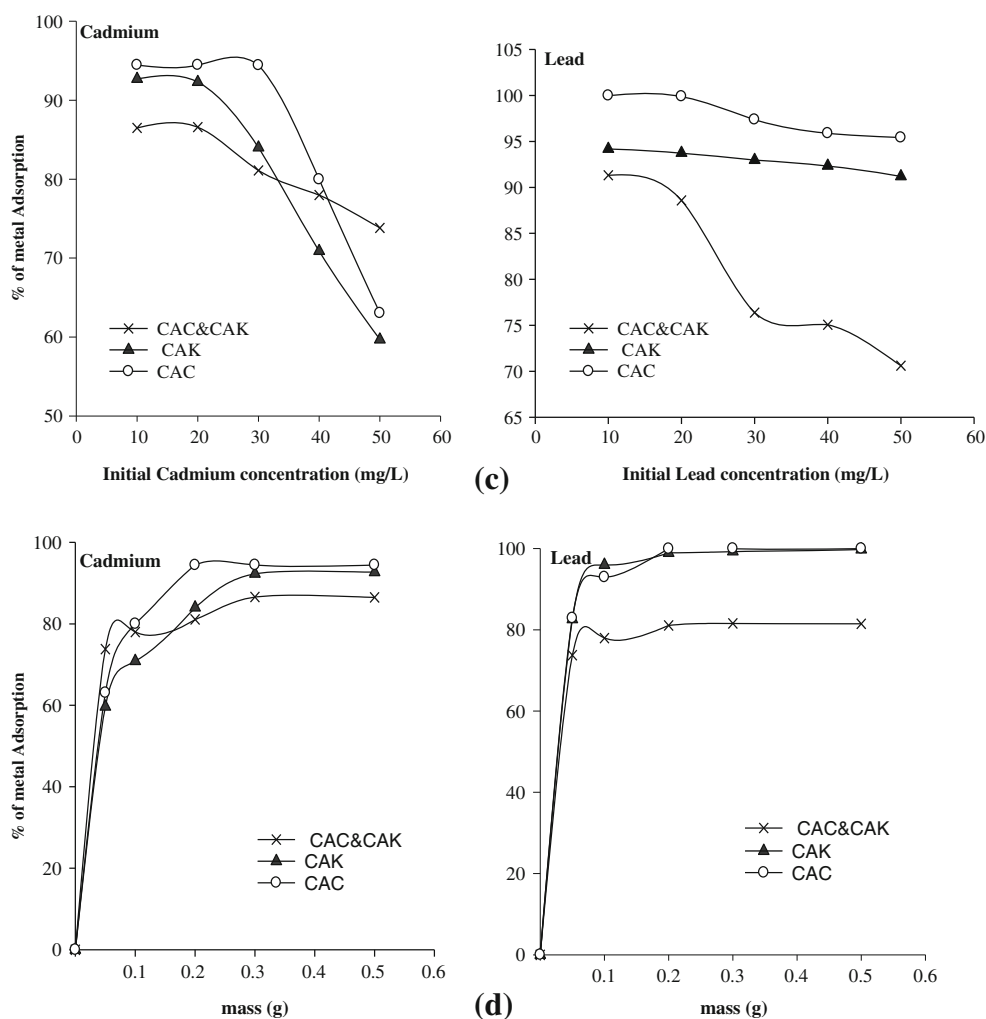
The adsorption percentages remained constant at initial concentrations between 10 and 20 mg/L and decreased gradually with increasing initial concentrations between < 20 and 50 mg/L. These observations suggest saturation of active

binding sites of the carbons above initial metal concentrations higher than 20 mg/L.

Kinetic study

To investigate the adsorption mechanism and rate controlling steps, adsorption kinetic data were modeled using pseudo-first-order and pseudo-second-order equations. The results are shown in Fig. 3 and Table 3. For metal lead, the correlation coefficients (R^2) of the pseudo-second-order model were higher than the ones of the pseudo-first-order. There was a significant difference between the calculated equilibrium adsorption ($Q_{eq, cal}$) and experimental equilibrium ($Q_{eq, exp}$) adsorption capacities obtained by the pseudo-first-order model, while a relatively small difference was observed between $Q_{eq, cal}$ and $Q_{eq, exp}$ obtained by the pseudo-second-order model. As for cadmium, the correlation coefficients (R^2) were close to 1, and the pseudo-second-order $Q_{eq, cal}$ and $Q_{eq, exp}$ rates were similar. On the contrary, the pseudo-first-order model $Q_{eq, cal}$ and $Q_{eq, exp}$ rates were not close to each other for metal

Fig. 2 Effect of initial concentration (c) and effect of adsorbent mass (d) on Pb(II) and Cd(II) ion removals



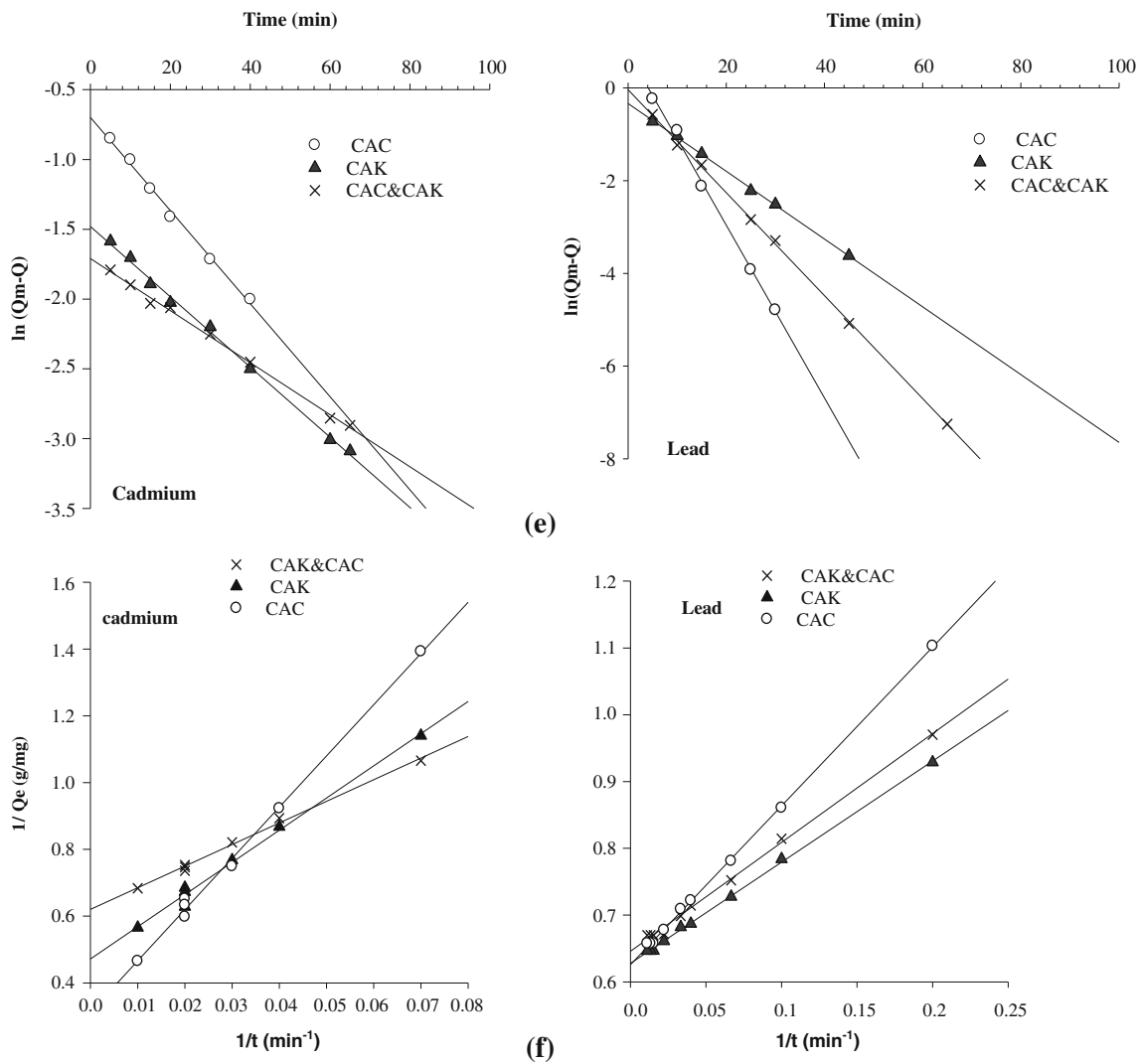


Fig. 3 Pseudo-first-order (e) and pseudo-second-order (f) kinetic fits for adsorption of Pb(II) and Cd(II) ions on CAC, CAK, and CAC and CAK (1:1)

cadmium. Therefore, the adsorption of lead and cadmium on cashew nuts, shea nuts, and the mixture of cashew and shea nuts can be described as by pseudo-second-order

kinetic model. That indicates that a chemo-sorption is the limiting factor which involves electron exchange between lead and cadmium, and low-cost adsorbents.

Table 3 Pseudo-first-order and pseudo-second-order kinetic parameters for Pb(II) and Cd(II) sorption on CAC, CAK, and mixture CAC and CAK

Element	Absorbent	$Q_{eq, exp}$ (mg/g)	Pseudo-first-order				Pseudo-second-order			
			$Q_{eq, cal}$ (mg/g)	K_{ad1} (/min)	R^2	Δqm (%)	$Q_{eq, cal}$ (mg/g)	K_{ad2} (g/mg/min)	R^2	Δqm (%)
Pb	CAC	1.60	13.25	0.33	0.84	1165	1.87	0.09	0.99	27
	CAK	1.53	0.54	0.04	0.89	99	1.49	0.33	0.91	4
	CAC and CAK	1.49	7.53	0.11	0.78	604	1.72	0.05	0.98	23
Cd	CAC	1.56	0.97	0.09	0.99	59	1.69	0.15	0.97	13
	CAK	1.58	1.01	0.06	0.99	49	1.57	0.15	0.94	1
	CAC and CAK	1.33	0.67	0.08	0.83	66	1.61	9.68	0.85	28

$Q_{eq, exp}$ experimental equilibrium adsorption; $Q_{eq, cal}$ calculated equilibrium adsorption capacity

Adsorption isotherms

The Langmuir and Freundlich isotherms and their parameters are shown in Fig. 4 and Table 4, respectively. The experimental data for lead(II) and cadmium(II) ions adsorption on cashew nut shell activated carbon CAC were better described by the Freundlich isothermal model. This is confirmed by the high correlation coefficient values ($R^2 = 0.95$ for lead and $R^2 = 0.99$ for cadmium). As for the shea nut shell activated carbon CAK, lead adsorption was better described by the Langmuir model ($R^2 = 0.98$), while cadmium adsorption was by the Freundlich model ($R^2 = 0.99$). Table 5 also indicates that Langmuir model best fitted lead and cadmium adsorptions by the mixture of the two activated carbons (CAC and CAK) than the Freundlich model. CAK removed efficiently lead and cadmium from aqueous solutions than CAC and the mixture CAC and CAK, indicated by higher lead and cadmium maximum amount (Q_m) obtained with CAK (Table 4). The mixture of CAK and CAC resulted in higher Q_m

values of lead and cadmium than using CAC alone. Q_m followed the order Q_m (CAK) > Q_m (CAC and CAK) > Q_m (CAC). Therefore, adsorbent removal capacity can be improved by mixing two adsorbents. With respect to the Langmuir equilibrium parameter (R_L), the values obtained with all activated carbons ranged between 0 and 1, indicating that the isotherm is favorable. The maximum amount (Q_m) obtained by Langmuir model indicated that CAC, CAK, and the mixture CAC and CAK can be used to remove lead and cadmium from wastewater or contaminated drinking water. However, the Q_m values obtained with CAC from this study are much lower than those reported by Kumar et al. (2012) and Coelho et al. (2014) (Table 5). Moreover, the Q_m values of Cd(II) and Pb(II) for CAC, CAK, and CAK and CAC measured in the present study were lower than the ones of most sorbents (Gaya et al. 2015; Adebisi et al. 2017) (Table 5). These observations show that Q_m is not the sole factor driving removals of Cd(II) and Pb(II) ions from aqueous solutions by biosorbents.

Fig. 4 Linearized Langmuir (g) and Freundlich (h) adsorption isotherms for Pb(II) and Cd ions on the CAC, CAK, and CAC and CAK (1:1)

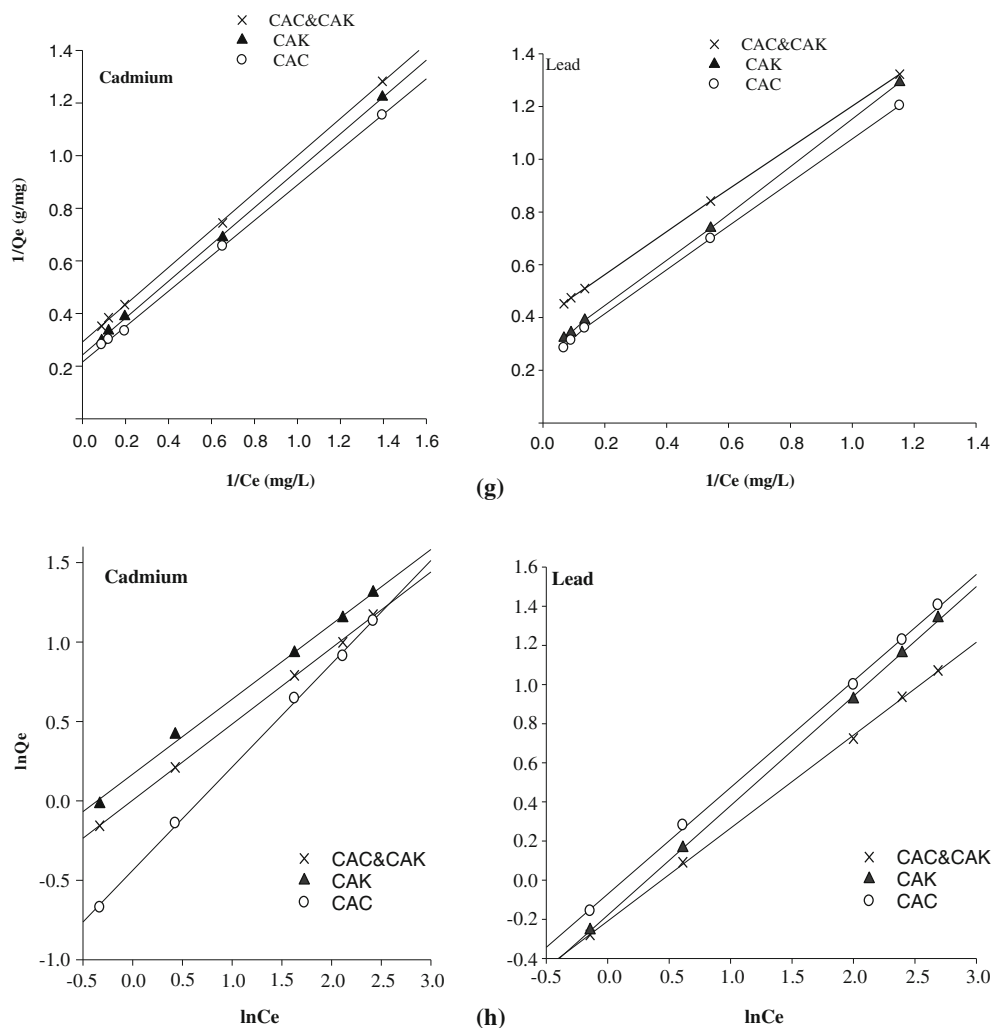


Table 4 Langmuir and freundlich isotherm parameters for Cd(II) and Pb(II) ions sorption on CAC, CAK, and mixture CAC and CAK

Element	Adsorbent	Freundlich			Langmuir			
		R^2	$K_f [(mg/g) (L/mg)_n^{-1}]$	N	R^2	$Q_m (mg/g)$	b	R_L
Cd	CAC	0.99	2.560	3.310	0.95	2.87	14.31	0.0035
	CAK	0.99	1.068	1.380	0.98	5.46	0.261	0.1610
	CAC and CAK	0.95	1.030	2.090	0.98	3.63	0.39	0.1140
Pb	CAC	0.95	0.087	5.631	0.91	2.61	479.2	0.0001
	CAK	0.92	1.330	1.278	0.98	16.1	0.088	0.3620
	CAC and CAK	0.91	0.925	2.439	0.96	3.06	0.395	0.1120

Application to natural freshwater

The optimum conditions for removals of lead and cadmium from a 20 mg/L synthetic aqueous solution were pH 5 and biosorbent mass dose of 12 g/L. At that level, the lead and cadmium removal efficiencies ranged between 95 and 99% for CAC and CAK, and 81–86% for mixed CAC and CAK. We applied the activated carbons to typical freshwater in the aforementioned optimal conditions. The results are shown in Fig. 5. Relatively lower removal efficiencies were found for natural freshwater compared to synthetic aqueous solutions: 61–70% for CAC and CAK, and 67–68% for mixed CAC and CAK. Nevertheless, it should be noted that the removal percentages obtained in the typical freshwater were relatively high. Some studies have successively applied activated carbon prepared from biomaterials to the removal of trace metals from real wastewaters (Abdelfattah et al. 2016; ALOthman et al. 2016; Khademi et al. 2015). However, little information exists for natural freshwater, especially for Cd and Pb. Kazemipour et al. (2008) found lower Zn and Cu removal efficiencies by almond nut activated carbon in real wastewater (5–9% less) compared to synthetic wastewater. They related the lower removal efficiency to other components present in the real wastewater, as well as initial Zn and Cu concentrations. Their finding supports results from this study. The lower removal

efficiencies found for typical freshwater in comparison to synthetic water in the present study suggest that other factors such as organic matter, nitrates, and other trace metal concentrations may compete with lead and cadmium for binding to the adsorption sites of the activated carbons. On the other hand, Minamisawa et al. (2004) removed Cd(II) and Pb(II) ions from rainwater and river water at higher rate (97–102%) compared to our results, using biosorbents other than activated carbons (e.g., prewashed and dried coffee beans). Our results also showed that increasing the biosorbent mass dose from 12 to 18 g/L increased the removal efficiencies by 9–15% even at higher lead and cadmium concentrations (30 mg/L). These results evidence that the cashew nut shell and shea nut shell activated carbons can successfully remove cadmium and lead from natural freshwater.

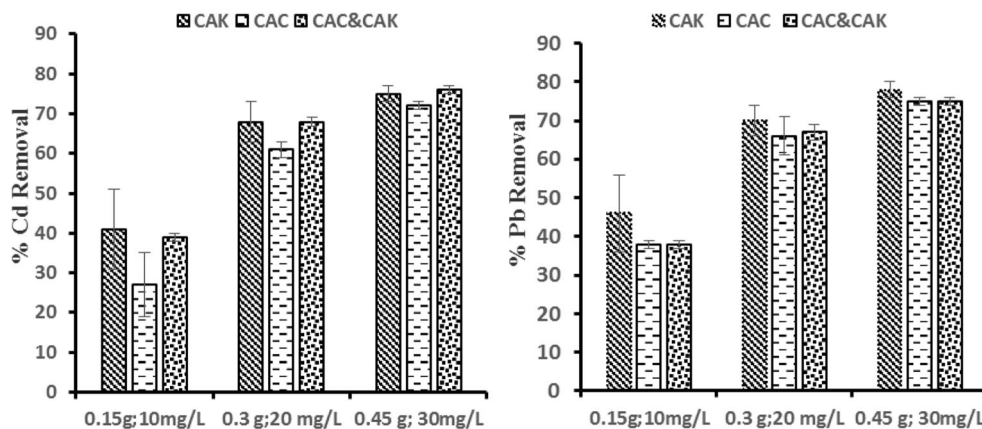
Cost estimation for CAC and CAK production

The production cost estimation includes raw material transportation, chemicals (sodium hydroxide), packaging, and electricity usage fees (Table 6). About 20 h and 10 h were required to obtain 1 kg of cashew nut shell and shea nut shell activated carbons, respectively. The electric furnace consumed 2 kWh of energy. The electricity rate is 0.12 US\$/kWh in Cote d'Ivoire. About 20 L of waters was necessary to prepare 1 kg of cashew

Table 5 Comparison of Langmuir constant (Q_m) with data from literature for lead(II) and cadmium(II) ions

Heavy metal Adsorbents	Lead $Q_m (mg/g)$	Cadmium $Q_m (mg/g)$	Reference
Coconut shell	151		Song et al. (2014)
Cashew nut shell	28.6	11.2	Coelho et al. (2014)
Palm oil mill effluent	94.3		Adebisi et al. (2017)
Doum palm shell	500	100	Gaya et al. (2015)
Cashew nut shell		22.1	Kumar et al. (2012)
Lemon cortex		12.0	Kelly-vargas et al. (2012)
CAK	16.1	5.46	This work
CAC and CAK	3.46	3.06	This work
CAC	2.61	2.87	This work

Fig. 5 Removal of cadmium and lead ions from spiked surface waters collected from the Cavally River



nut shell and shea nut shell activated carbons. Overall, the production of cashew and shea nut activated carbons costs was estimated to be about 16.0 US\$/kg and 13.6 US\$/kg, respectively (Table 6). These costs were significantly lower than the production cost (58.39 US\$/kg) of activated carbon prepared by Kouakou et al. (2017) using *Ricinodendron heudelotii* from Cote d'Ivoire. The power consumption of the preparation process of this study was much lower than the one (61.6 kWh/kg) calculated by Alslaibi et al. (2014) during activated olive stone waste carbon preparation. It can be concluded that the activated carbons made from Cashew nut and Shea nut shells are commercially competitive for removing lead and cadmium ions from water. The cashew nut and shea nut shells activated carbons can be used for the manufacturing of cheaper generation of filters that will be used by wastewater treatment plants, drinking water production companies, and by large section of the population. Keeping in mind that this study focused only on adsorption processes, further studies on desorption processes should be conducted to elucidate and find out alternatives for regeneration and phase separation issues.

Conclusion

The cadmium(II) and lead(II) ion sorption on activated carbons prepared from cashew nut shell CAC and shea nut shell

CAK, and their mixture CAC and CAK in synthetic aqueous solutions and typical freshwater were investigated in this study. The results showed that the cashew and shea shells, and their mixture can be successfully used as adsorbents for the treatment of aqueous solution contaminated with lead and cadmium. The removal rates ranged between 94.14 and 99.9% for lead and between 86.5 and 94.46% for cadmium, at the optimal adsorption conditions of pH 5.0, adsorbent dose mass 12 g/L and initial metal concentration of 20 mg/L. Isotherm modeling investigated through the Langmuir and Freundlich models revealed that Langmuir model well described lead and cadmium adsorption by the mixture of the two activated carbons (CAC and CAK). The Langmuir and Freundlich models best fitted the isotherms of Pb(II) ions adsorbed by CAK and CAC, respectively. The equilibrium adsorption data of cadmium were found to be described by Freundlich isotherm model. The maximum loading capacities (Q_{max}) of Cd obtained from the Langmuir isotherm were 2.87 mg/g, 3.46 mg/g, and 5.46 mg/g with CAC, CAC and CAK, and CAK, respectively, while those of Pb were 2.608 mg/g, 3.06 mg/g, and 16.103 mg/g with CAC, CAC and CAK, and CAK, respectively. Furthermore, kinetic adsorption study followed the pseudo-second-order for the studied metals, indicating that the limiting factor which involves electron exchange between lead and cadmium, and low-cost adsorbents is a chemo-sorption. The cashew and shea nut

Table 6 Estimated production cost of cashew and shea nut shells activated carbon (US\$/kg)

Component	Cashew Input and Consumption	Cashew Estimated cost	Shea nut Input and Consumption	Shea nut Estimated cost
Raw material collection and transportation	–	3.60	–	3.60
Sodium hydroxide	200 g	5.62	200 g	5.62
Power consumption	40 kWh	4.82	20 kWh	2.41
Packaging	–	1.98	–	1.98
Distilled water	0.02 m ³	0.01	0.02 m ³	0.01
Total estimated cost		16.0		13.6

shells along with their mixture showed both commercially competitive and great potentials for efficient treatment of cadmium and lead-contaminated waters. The activated carbons prepared from cashew nut shell CAC and shea nut shell CAK, and their mixture CAC and CAK can be used for the manufacturing of cheaper generation of filters that will be used by wastewater treatment plants, drinking water production companies, and by a large section of the population.

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