



Arsenic Removal from Water by Adsorption using Low Cost Activated Carbon Prepared from Local Wastes

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Abstract The present study concerns arsenic removal from water using activated carbon prepared from Shea cake (CAK). The activated carbon CAK has the following characteristics: BET surface area is equal to 1,148 m²/g and the pore volume to 0.607 cm³/g. This activated carbon is essentially microporous with the volume of micropores representing over 70% of the total pore volume. The "batch method" was used for arsenic removal and it revealed that the contact time value was equal to 90 min. Kinetic models such as pseudo first-order and pseudo second-order were used to evaluate the mechanism of arsenic adsorption on activated carbons. Arsenic removal process was found to be governed by first-order kinetic. The Langmuir and Freundlich isotherm models agreed with experimental data. The maximum adsorption capacity obtained using Langmuir isotherm model was 7.87 µg/g.

Keywords activated carbon, CAK, adsorption isotherms, arsenic, initial concentration, surface area

1. Introduction

In the current context with fast population growth, increased use of energy resources and the pervasiveness of consumers increasing industrial and household waste, waste disposal becomes more cumbersome. Therefore, the global interest in preserving the environment has attracted the attention of researchers in finding the technical means to exploit this waste. Several ways of recovering waste have been developed in recent years. For example, the recovery of waste for the production of energy, for composting, for the preparation of activated carbon, etc. [1-5]. Activated carbons are inexpensive materials, which can be obtained by carbonization and activation of precursors already containing a large amount of carbon and a small percentage of inorganic matter [7]. Different studies have been devoted to the production and characterization of activated carbons from materials from different plant sources such as date nuclei [8-9]. Inorganic compounds (arsenic, fluorine, heavy metals, nitrates and phosphates, etc.), mainly from agriculture, industry and domestic effluents also attract the attention of those involved in the management of aqueous environment. They cause problems, both in terms of the degradation of environment resulting from an invasion by plants (eutrophication) as well as the complications they generate during the production of drinking water. The arsenic element historically undesirable has many effects on man: skin lesions, gangrene, cardiovascular and pulmonary diseases,



hypertension and cancers. High concentrations may cause arsenicosis [10]. There have been cases of poisoning of arsenic in Bangladesh. Therefore, WHO and the US Environmental Protection Agency (US EPA) have changed the CMA from 50 to 10 µg/L [11, 12]. Between 10 and 13 µg/L, some exceptions are possible, but with a limited duration and restrictions of use [13]. Thus the analytical techniques must be adapted in order to obtain limiting fuses (10 µg/L). Due to its toxicity and the modification of the standard, it is essential to control the various routes of arsenic removal. Similarly, to deal with the pollution due to inorganic compounds, several methods of decontamination have been developed. Examples include the removal of nitrite ions by the use of an electroactive conductive polymer [14], and removal of arsenic by nano filtration, ion exchange, and adsorption on activated aluminum [15]. The purpose of this study was to characterize the performance of activated carbon prepared from Shea cake and named CAK with respect to the adsorption of arsenic. The influences of contact time and activated carbon assay on the adsorption of arsenic have been studied, and equilibrium adsorption isotherms have been established.

2. Materials and methods

2.1. Activated Carbons

2.1.1. Preparation of activated carbon

Activated carbon CAK was prepared from shea cake. The synthesis of activated carbon was performed as follows: the precursors were riddled to obtain particles with diameter less than or equal to 0.8 mm, then impregnated for 6 hours in 40% phosphoric acid. The ratio of impregnation (mass of acid/mass of precursor) was 1.5. The activated carbon was obtained by carbonization of the impregnated material at 450 °C for 2 hours [16]

2.1.2. Characterization of activated carbon

Chemical characteristics (chemical surface functions, pH of zero charge) of the synthesized activated carbon were determined by Boehm titrations [17, 18] and the method of Lopez- Ramon et al. respectively [19]. Nitrogen isotherms were measured using an ASAP 2010 (Micromeritics) at 77 K. The Brunauer, Emmett and Teller (BET) surface areas of the samples were determined by nitrogen adsorption–desorption isotherm measurement. These isotherms were then used to calculate total pore volume (Vp). The size distribution of pores, the micropore and mesopore volumes were obtained by Density Functional Theory (DFT). The size distribution of pores was also obtained by Barrett-Joyner and Halenda (BJH) model.

2.2. Arsenic analysis by molecular absorption spectrometer

Distilled water (conductivity: 1-3 µS/cm) was used to prepare the arsenic solution. The concentrations of arsenic before and after adsorption were measured using a UV–Vis spectrophotometer (Shimadzu). For arsenic analysis, the standard method AFNOR [20] was modified allowing the analysis of low concentrations.

2.3. Arsenic Adsorption Studies

Adsorption of arsenic on activated carbon was carried out in batch mode using 100 mL Erlenmeyer flasks at ambient temperature (29 ± 2 °C). Each flask was magnetically stirred at 300 rpm. The effects of contact time, amount of activated carbon and initial concentration of the solution have been studied. After equilibration, the solution was filtered through a membrane filter (pore size 0.45 µm) and the filtrate was used for absorbance measurement. The amount of arsenic adsorbed, Q_e (µg/g), was calculated from the formula:

$$Q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where Q_e is the amount adsorbed, V (mL) is the volume of the liquid phase, C_0 (µg/L) the initial concentration of the solute, C_e the concentration of the solute at equilibrium, and m (g) the amount of the adsorbent used.

2.3.1. Influence of contact time

1 g of activated carbon was used to study the effect of contact time during adsorption of the target pollutant. 100 mL of the arsenic solution at a concentration of 75 µg/L were prepared for this experiment. The flask provided with arsenic solution and activated carbon was kept in constant agitation at ambient temperature. At regular intervals, samples were taken for absorbance measurement. The adsorption capacity at every time, Q_t (µg/g) of each dye was calculated using the relation:



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

where C_t ($\mu\text{g/L}$) represents the concentration of the arsenic at each time t (min), V (mL) the volume of the liquid phase, C_0 ($\mu\text{g/L}$) the initial concentration of the solute, and m (g) the amount of the adsorbent used.

2.3.2. Effect of activated carbon amount

Different amounts of activated carbon (0 to 4 g) were dispersed in 100 mL of the arsenic solution, of which the concentrations were the same in each flask (75 $\mu\text{g/L}$). The pH was adjusted to be the same at the beginning. The mixture was stirred until equilibrium time and then a sample was taken for analysis.

2.3.3. Effect of initial concentration

The effect of initial concentration on the adsorption process of arsenic has been studied by varying the initial concentration of the solution from 0 to 50 $\mu\text{g/L}$ under the same conditions by a constant amount of the adsorbent.

3. Results and Discussion

3.1. Physicochemical characteristics of activated carbon CAK

The characterization experiments conducted on activated carbon showed that the pH of zero charge (pHZC) was 6.8 (slightly acidic). According to Boehm titration, the surface function groups are more acidic than basic. The result revealed that the concentration of acidic functions was 6.2 meq/g, while the concentration of basic functions was 1.2 meq/g.

The structural parameters calculated from nitrogen adsorption isotherms are presented in Table 1.

Table 1: Structural parameters of activated carbon calculated

Parameters	CAK
Yield (%)	32.5
Surface area (S_{BET}) m^2/g	1,148
Micro-pore surface area (S_{mic}) m^2/g	1,005
Total pore volume (V_p) cm^3/g	0.607
Micropore volume cm^3/g	0.435
Mesopore Volume cm^3/g	0.172
Average diameter of pore by BET \AA	21.16

The data clearly show that the CAK sample had a large surface and big volume of micropores. Based on the ratio of the volume of micropores to the total pore volume, CAK can be described as predominantly microporous of about 70%. The value of the specific surface area of CAK obtained is similar to those obtained by Emine et al [21]. However, other researchers obtained the values of specific surface area of activated carbons, which were much greater than our ones [22, 23]. CAK has an average diameter of pores (determined by BET) that are relatively small, almost at the limit of the microporosity. This result is in agreement with those obtained by other researchers [8, 24] as shown in Table 2. The differences come probably from the differences in precursors used and the preparation methods applied.

Table 2: Comparison of textural characteristic of CAK to those in the literature

Adsorbents	TC ($^{\circ}\text{C}$)	Activation	SBET (m^2/g)	References
Activated carbon «CA-K»	450	H_3PO_4	1,148	--
Mineral activated carbon of Algeria « Ménouna »	800	KOH	1,241	[24]
Activated carbon prepared from date stones	500	KOH, NaOH, H_3PO_4	1,400	[23]
Activated carbon derived from rice straw	450	KOH	1,554	[22]
Activated carbon derived from waste of tea	350	H_3PO_4	1,157	[21]
Activated carbon prepared from jute sticks	750	Physical activation	452-724	[25]



3.2. Adsorption of arsenic on CAK

3.2.1. Influence of contact time

Figure 1 shows the kinetic of arsenic adsorption on CAK. The adsorption of arsenic is fast in the first 25 minutes, and then gradually slows down until equilibrium is reached after 90 min, corresponding to about 70% removal of arsenic ($C_0 = 75 \mu\text{g/L}$). So, 50% of the arsenic was removed after 25 minutes.

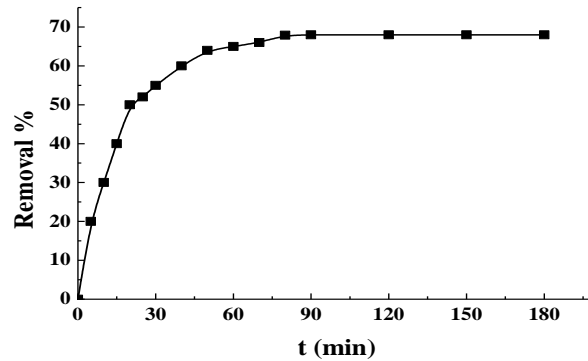


Figure 1: Effect of contact time on adsorption of arsenic on CAK ($C_0 = 75 \mu\text{g/L}$, $V = 100 \text{ mL}$, natural pH, $m_{CA} = 2 \text{ g}$)

The results show that the adsorption is rapid in the first few minutes of contact, and then gradually slows down until it reaches equilibrium. Indeed, the rapid adsorption in the first minutes maybe due to the existence of a large number of adsorption sites available initially. Over time, this number decreases, making access difficult for the remaining sites due to repulsion between the solute molecules from the liquid phase and those already adsorbed on the activated carbon. This is what explains the slowdown in the adsorption before reaching equilibrium. The equilibrium time did not allow sufficient removal of arsenic

3.2.2. Influence of the initial concentration on the removal of arsenic

Figure 2 A shows the influence of the initial concentration on the removal of arsenic. The adsorption of arsenic increases with the initial concentration. The residual concentration was plotted versus initial concentration (Fig. 2 B). The obtained curve shows that below $35 \mu\text{g/L}$ as initial concentrations of arsenic, the residual concentration remains below $10 \mu\text{g/L}$ (minimum allowable concentration according to the WHO and US EPA).

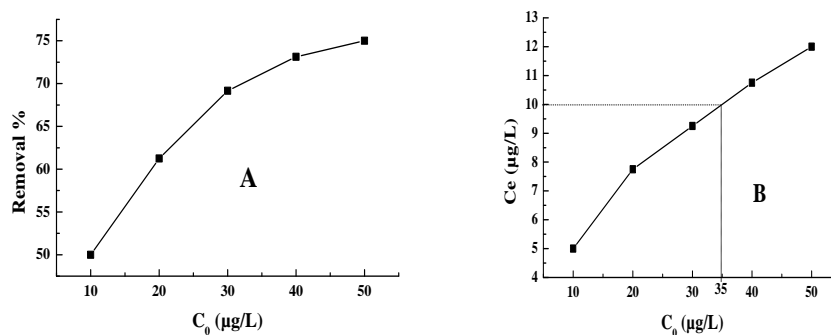


Figure 2: Influence of initial concentration on adsorption of arsenic (A), and on the value of the residual concentration of arsenic (B) on CAK ($V = 100 \text{ mL}$, natural pH, $m_{CA} = 2 \text{ g}$, $t = 120 \text{ min}$)

The initial concentration of arsenic provides an important driving force to overcome mass transfer resistance of the pollutant between the aqueous phases and the solid phase. Thus, for a higher initial concentration, the number of molecules competing for the available sites on the surface of the activated carbon becomes larger. Therefore, the maximum adsorption capacity of arsenic becomes larger.



3.2.3. Effect of amount of CAK on the removal of arsenic

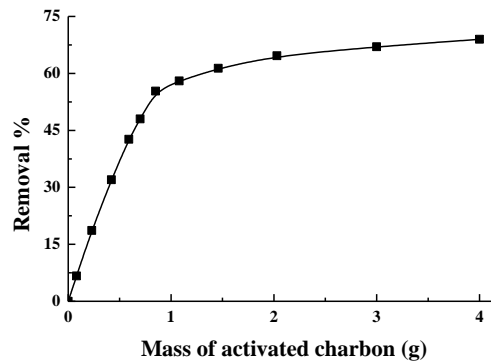


Figure 3: Influence of mass of adsorbent on adsorption of arsenic ($C_0=75 \mu\text{g/L}$, $V = 100 \text{ mL}$, natural pH)

The amount of CAK was varied from 0 to 4 g and the concentration of arsenic was fixed at $75 \mu\text{g/L}$. The Figure 3 shows the effect of the mass of CAK on the percentage removal of arsenic. The result shows that removal percentages increase as the amount of CAK increases as well. However, below 1 g of CAK, the removal rate of arsenic is low. With 4 g of activated carbon, the removal of arsenic was about 70%.

3.2.4. Study of adsorption isotherms

Adsorption isotherm is obtained by plotting Q_e versus C_e (Fig. 4). The result shows that the adsorption isotherm of arsenic on activated carbon CAK is type H (Freundlich) but also approximates type L (Langmuir).

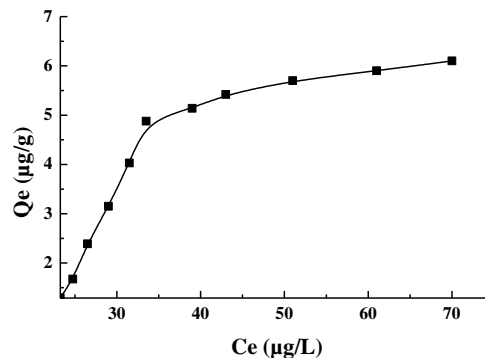


Figure 4: Isotherm adsorption of arsenic from solution ($C_0=75 \mu\text{g/L}$, $V = 100 \text{ mL}$, natural pH)

Langmuir and Freundlich Isotherms are used to describe the nature of the adsorption equilibrium. The model of Langmuir is most frequently used for the adsorption of pollutants in solution. The Langmuir isotherm can be modeled by the equation:

$$Q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (3)$$

Where Q_e is the amount of pollutant adsorbed at equilibrium per unit mass of the adsorbent ($\mu\text{g/g}$), Q_0 is the adsorption capacity at saturation ($\mu\text{g/g}$), C_e is the concentration of pollutant at equilibrium and K_L ($\text{L}/\mu\text{g}$) is the adsorption equilibrium constant.

In the case of an adsorbent with a heterogeneous adsorption surface (adsorption sites energetically different), Freundlich model is used to characterize the adsorption. The Freundlich equation is given by:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

where Q_e (mg/g) is an amount adsorbed, C_e (mg/L) is the equilibrium solution phase concentration recalculated per unit mass of carbon, n (dimensionless) is the empirical parameter that represents the heterogeneity of the site energies, and K_F is Freundlich adsorption coefficient.



Table 3 presents the parameters fitting the experimental data to the Langmuir and Freundlich equations. (Figure not shown here.) The results indicate that adsorption of arsenic on the activated carbon CAK follows mainly the Freundlich isotherm, as indicated by the high value of the correlation coefficient ($r^2 > 0.99$), but also also Langmuir isotherm ($r^2 > 0.96$). A low value of capacity factor, $K_F < 2 \mu\text{g/g}$, during the adsorption of arsenic according to Freundlich model indicates a lower affinity of arsenic to the activated carbon CAK. The value of average energy of site ($n = 3.32$) satisfies the heterogeneity condition ($1 < n < 10$). But the value of the maximum adsorption capacity Q_0 is very low ($< 8 \mu\text{g/g}$).

Table 3: Parameters fitting the experimental data of Freundlich and Langmuir Isotherms

Freundlich			Langmuir		
n	K_F	r^2	Q_0	K_L	r^2
3.32	1.71	0,963	7.94	0.049	0.998

4. Conclusions

This study shows that activated carbon CAK prepared from Shea cake can be used for an efficient removal of arsenic from water. CAK has a high surface area ($1,148 \text{ m}^2/\text{g}$). Equilibrium and kinetic studies were made for the adsorption of arsenic from aqueous solutions on CAK in the concentration range $0 - 75 \mu\text{g/L}$. Under the conditions tested ($C_0 = 75 \mu\text{g/L}$, $V = 100 \text{ mL}$, natural pH, dosage of adsorbent 2 g), the equilibrium time was 90 min . The Freundlich equation showed a somewhat better fit than does the Langmuir equation for adsorption of arsenic using CAK as activated carbon. On the basis of studies reported, the activated carbon CAK has been successfully used already as adsorbent for the removal of arsenic from aqueous solutions. This is so an alternative of green chemistry to reuse carbon containing residues for useful purposes.

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