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Preparation of activated carbons from safou and avocado seeds: Study of the adsorption of chromium (VI)

Préparation de charbons actifs à partir de noyaux de safou et d'avocat : Étude de l'adsorption du chrome (VI)

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ABSTRACT:

The aim of this study is to study the performance of the removal of chromium (VI) in water by using activated carbon from safou and avocado seeds (CA-Sa and CA-Av). The obtained activated carbon had specific areas of 2.903 m²g⁻¹ for CA-Sa NaOH, 2.103 m²/g for CA-Sa ZnCl₂ and 1.46 m²g⁻¹ for CA-Av ZnCl₂. Various parameters such as the mass of activated carbon, the pH of the solution, the contact time and the initial concentration were studied to establish the optimal conditions for chromium (VI) adsorption on these charcoals. The results showed that at pH 2.48 elimination of chromium (VI) in aqueous solution is favorable and the adsorption rate of chromium (VI) increase with the increase the mass of activated carbon. At a certain mass threshold, the adsorption decreases due to the saturation phenomenon. The kinetics of adsorption is second order and the maximum adsorption capacity of chromium were respectively 99.28; 99.00 and 82.92 mg/L for CA-Sa $ZnCl_2$, CA-Av $ZnCl_2$ and CA-Sa NaOH, in aqueous solution for concentrations of 2.68 to 147.32 mg/L.

Keywords: Safou, Avocado, Actived carbon, Chromium (IV).

RÉSUMÉ

La pollution des eaux par des métaux lourds et des micropolluants tels que le chrome, requiert des procédés très performants. L'utilisation des charbons actifs dans ce travail (CA-Sa et CA-Av) préparés à partir des amandes de safou et d'avocat, a été testée pour évaluer la capacité d'élimination du chrome en solution aqueuse. Le but de cette étude étant d'étudier la performance d'adsorption de ces charbons actifs. Les charbons actifs préparés ont des surfaces spécifiques de 2,903 m²g-1 pour CA-Sa NaOH, 2,103 m²/g pour CA-Sa Zncl₂ et 1,46 m²g⁻¹pour CA-Av Zncl₂. Divers paramètres tels que la masse de charbon, le pH de la solution, le temps de contact et la concentration initiale ont été étudiés pour établir les conditions optimales d'adsorption du chrome sur les charbons. Les résultats ont montré qu'à pH acide (2,48) l'élimination du chrome en solution aqueuse est très favorable et que les taux d'adsorption du chrome augmentent avec l'accroissement de la masse de charbon mais à un certain seuil de masse, l'adsorption décroit et ceci pourrait être dû au phénomène de saturation. La cinétique d'adsorption est de pseudo second ordre et la capacité d'adsorption maximale du chrome a été respectivement de 99,28 ; 99,00 mg/L pour le CA-Sa Zncl₂, CA-AvZncl² et 82,92 CA-Sa NaOH en solution aqueuse pour des concentrations de 2,677 à 147,32 mg/L*.*

Mots clés : Safou, Avocat, Charbon actif, Chrome (IV).

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1. INTRODUCTION

Currently, given the human activities which cause a huge imbalance on nature by creating considerable damage on the environment, the protection of the environment has become a concern and a major challenge of our society. Cameroon in its logic of industrial development, encourages expansion and development in this sector, however this contributes to increase the flow of waste. It is therefore necessary to find adequate solutions to reconcile development with environmental policies. For example, mining activities lead to the release of chemical elements buried for years in rocks which modify the constitution of environment (surface and underground water, soil, air, etc.), causing temporary or permanent pollution. The prevention and management of this environmental degradation caused by certain heavy metals such as chromium, lead, copper from industrial waste and particularly corporate wastewater. Several studies have been carried out on the treatment of wastewater, particularly depollution of heavy metals. Water is indeed one of the main way of contamination of the environment by metals. Chromium, especially Cr (VI), which is found in wastewater from the leather and steelmaking industries, is a health hazard. It is considered as a serious problem because of its toxicity and bio-accumulation. It is dangerous as for human health as it is for fauna.

There are several physical methods based on adsorption (Ahmad et al., 2012). Activated carbon and clays are the most used to date because of the availability of the local material used (Fotio et al., 2005). Many research have been focused on the exploitation of waste into adsorbents for the removal of metals in contaminated water. For example, with the production of activated carbon from wood chips, coconut shells, corn cobs and sweet banana peelings (Kamga, 2014). Safou and avocado are highly appreciated fruits in Cameroonian cities and towns, consumed on streets and in households, thereby releasing significant waste. This situation is particular to the city Ngaoundere where we have sampled our seeds. This paper is a contribution to the valorization of seeds by manufacturing activated carbon for wastewater treatment.

2. MATERIAL AND METHODS

2.1. Material

The basic material for carrying out this work consists in a sample of safou and avocado seeds (Figure 1) collected in Ngaoundere (Cameroon) and a sample of a synthetic aqueous solution of chromium (VI).

2.2. Methods

2.2.1. Preparation of the stock solution of chromium (VI)

The chromium (VI) solution at 150 mg. L^{-1} was prepared by dissolving an appropriate amount of potassium dichromate reagent $(K_2Cr_2O_7)$ in 1000 mL of distilled water. The initial concentrations of Cr (VI) ions varying from 30 to 120 mg.L-1 were prepared with extremes of 2.67 and 147.32 mg/L.

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2.2.2. Preparation of adsorbents (active carbon)

After the seeds were collected and washed, they were dried in an oven (brand BINDER) for 24 hours. The seeds were grinded and sieved by using a 500 μm AFNOR sieve. After these pretreatment steps, we continued with the activation steps (acids and bases). The acid chemical activation was obtained at room temperature with $ZnCl₂$ at 250 rpm for 5 h. The contact time was 5 h, with the increase of temperature from 85 °C to 100 °C. The mixture was placed in the oven for 24 h at 110 °C. 20 g of each sample activated by $ZnCl₂$ were placed in a calcination oven at 400 °C for 1 h 30 min. The product obtained was washed with cold water several times with stirring for 15 minutes. It is then mixed with 250 mL of a hydrochloric acid solution (3M) and stirred for 10 minutes, separate from the supernatant. The same operation was repeated for 2 h. The obtained product was then washed with hot distilled water with stirring for 15 minutes, and with cold distilled water and also stirred for 15 minutes. The products were dried at 110 °C, crushed and sieved. The samples obtained are noted: Seeds of safou and avocado (CA-Sa and CA-Av).

As for basic chemical activation, using solid NaOH, the process is the same as with $ZnCl_2$, except for the washing of the sample which is done for 24 h with continuous stirring at 150 rpm.

The final step was pyrolysis under a controlled atmosphere at 500 °C during 1 h 30 min. This allows the elimination of all volatile organic matter.

2.2.3. Characteristics of adsorbents

Residual humidity

The humidity is a ratio expressed as a percentage, it was determined by drying the adsorbent in an oven at 110 °C. The humidity rate $(Hr(\%))$ formula is:

$$
Hr\left(\frac{\%}{\right) = \frac{(M_2 - M_3)}{M_2 - M_1} \times 100\tag{1}
$$

Where M_1 is the initial mass of activated carbon used (crucible + sample) before oven in (g); M_2 , the mass of the sample and M_3 , the mass of the crucible filled after oven in (g).

Ash content

A 5g sample of the sample is dried in an oven at 105 °C for 24 h and then placed in a ceramic crucible. This crucible is introduced into an oven adjusted to 650 °C. is maintained for 3 h at this temperature. After cooling to room temperature, the crucible was weighed again.

The ash rate (% C) is calculated as follows:

$$
(\%C) = \frac{(M_{in} - M_{fin})}{M_{in} - M_{cr}} \times 100
$$
 (2)

Where Mi is the initial mass (crucible + sample) before carbonization (g); M_{fin} , The final mass (crucible + sample) after carbonization in (g) and M_{cr} , The mass of the empty crucible (g).

Specific surface

The principle of this method consisted in determining the necessary quantity of methylene blue, to form a monolayer on the surface of the sorbent.

A mass of approximately 1g of finely ground sample was mixed in a 100 mL beaker with 20 mL of distilled water and stirred for 5 minutes at 700 rpm on a magnetic stirrer. Then, 5 mL of methylene blue (10 g/L) were added using a graduated burette, the mixture was stirred at 400 rpm for one minute: Using a glass, a drop of the solution was taken and placed on wattman filter paper. The test is said to be "positive" if on the filter paper there is a blue central drop

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surrounded by a wet area tinted with blue and "negative" if there is a blue central drop surrounded by a colorless wet area. (AFNOR, 1992).

If the test is positive, then 1 mL of BM is removed 5 times every minute to confirm the result, if on the other hand the test is negative, 5 mL of BM are added again so on until the positive test is reached. Having obtained a positive test, the corresponding volume of BM is noted and the value with methylene blue is determined according to the formula:

$$
VBS = \frac{v}{m}100\tag{3}
$$

Where v is the volume of BM corresponding to the positive test; the mass of biosorbent removed. We deduce the value of the specific surface according to the formula:

$$
SS = VBS \times 20.93. \tag{4}
$$

Methylene Blue Index

To determine the methylene blue index, we weighed 2g of activated carbon which we introduced into 100 mL of methylene blue solution with a concentration of 20 mg/L. After 15 minutes of stirring, we separated the carbon from the solution by filtration on a wahtman filter paper. From an atomic spectrometer, we determined the absorbance of methylene blue at the wavelength ($\lambda = 664$ nm), then we determined the residual concentration of methylene blue using the curve of calibration.

The methylene blue index or activated carbon adsorption capacity was calculated using the following relationship:

$$
Q_{BM} = \frac{(ci - ce)N}{m_{CA}} \chi M_{BM} \tag{5}
$$

Where Q_{BM} is apparent adsorption capacity (mg/g) of activated carbon vis-à-vis the adsorbate; Ci, initial concentration (mol/L) of the methylene blue (BM) solution; Cr, residual concentration (mol/L) of the BM solution; V, volume of the BM solution (100 mL); M_{BM} , BM molar mass (373.9 g/mol) and m_{CA} , mass (g) of activated carbon used.

Iodine index

The iodine index value was handled according to the procedure defined above. 10 mL of a 0.1N iodine and KI solution were taken and dosed with a 0.1 N sodium thiosulfate solution in the presence of two drops of starch poison playing the role of colored indicator until obtaining a colorless solution, which allowed us to have our volume of white. Then 0.05 g of each activated carbon distinctly were introduced into Erlenmeyer flasks containing before 15 mL of 0.1 N iodine solution, stirred for 4 min, filtered and measure out 10 mL of the filtrate with the sodium thiosulfate solution 0.1 N in the presence of two drops of starch.

The iodine value was calculated by the formula below:

$$
I_d = \frac{\left((V_b - V_s) \times N \times M_I \times \left(\frac{15}{10} \right) \right)}{m} \tag{6}
$$

Where (*Vb-Vs*) represents the difference in the results of the titration in the blank test and in the test with adsorbent in (mL of 0.1N sodium thiosulfate); *N*, normality of the sodium thiosulfate solution in (mol/L); *MI*, the atomic mass of iodine and m, the mass of the adsorbent in (g).

Determination of the point of zero charge pH (pH_{PZC})

The pH_{PZC} or pH of the zero-charge point corresponds to the pH value for which the net charge on the surface of the adsorbents is zero (Wibowo et al., 2007). This parameter is very important in adsorption phenomena, especially when electrostatic forces are involved in the mechanisms. A quick and easy way to determine the pH_{PZC} is to use the pH drift method which consists of placing 50 mL of 0.01 M NaCl solution in closed bottles and adjusting the pH of each (values between 2 and 12) by addition of NaOH or HCl solution (0.1 M). 50 mg of the sample of material to be characterized was then added to each flask. The suspensions were kept stirring at room temperature for 24h, and the final pH was then determined. The pH_{PZC} is the point where the final pH curve as a function of the initial pH intercepts the line final $pH =$ initial pH .

2.3. Experimental study

In order to carry out our experiments, we each took a precise mass m of activated carbon which we introduced into a beaker containing 100 mL of chromium (VI) solution prepared at a concentration which was also precise. Then we stir the mixture for 5 minutes before adjusting the pH, then leave it under stirring for a determined time. After stirring was complete, the mixture was allowed to sit for 5 minutes and then filtered. A volume of 5 mL of filtrate was removed for spectroscopic analysis.

3. RESULTS AND DISCUSSION

3.1. Physico-chemical characterization of the adsorbents

The results of the physico-chemical characterization of the adsorbents are presented in Table 1.

Sample	\rm{Hr} (%)	Ashes $(\%)$	$SS(m^2/g)$	IBM(mg/g)	Id(mg/g)	pHpz _C
$CA-Sa ZnCl2$	1.7	2	2.903	168.08	1130	2.7
$CA-Av ZnCl2$	2.1	4	2.013	143.83	1054	3.2
CA-Sa NaOH	1.9	\mathfrak{D}	1.46	119.04	761	7.4
CA-Av NaOH	2.3	3.1	-	94.45		

Table 1: Physico-chemical parameters of active carbon

The residual humidity of the samples varies from 1.7 to 2.3 with the values of the adsorbents prepared with the acid activator higher than those of the adsorbents prepared with the basic activator. This would show that the acid treatment would be better than the basic one. However, this rate is high for CA-Av compared to CA-Sa. This could be due to the different composition and structure of the material. Indeed, the organic composition of avocado seeds is more important than that of safou seeds. This logic can also be an explanation for the difference in the ash rate between avocado and safou-based activated carbon. Note that the charcoal prepared from safou seeds has a more porous structure than those from avocado seeds. Kafack (2014), which research was based on active carbon from peanut shells and jatropha wood, have found a residual moisture content of 0.76 % and a value of 30.21 % ash for charcoal activated with FeCl3. These values are much lower for our residual humidity values and higher with regard to ash (ours are between 2 and 4 %). This could be explained by the fact that the mineral content of materials used in this work is low compared to his. However, the values obtained by Babakhouya, 2010 (4.8 %; 4.9 %; 5.6 %) and Merzoug in 2014 (Hr = 4 %, $C = 2.12$ %) are very close to ours. We can also note that the adsorbents activated with

base have significant values of residual humidity and ash rate compared to those activated with acid, and this could be due to the fact that the base has not the ability to degrade the organic matter in our materials like acid.

Another information from this table 1 is that the activated carbon with zinc chloride $(ZnCl₂)$ has a large specific surface compared to the activated carbon with sodium hydroxide (NaOH). The iodine index test reveals a microporosity which varies from 1130 to 119.04 for the same precursor (safou) activated with acid ($ZnCl₂$) and (NaOH) respectively. The avocado seeds reveal the values of 1054 to 761 (mg/g) for the same tests. These values are close to those obtained by Babakhouya (2010) who obtains the values of 622.3 to 749.3 of iodine index, Kafack (2012) which obtains the iodine index values of 1239.94 for the acidic activated carbon H_3PQ_4 , 906.7 for the basic carbon (228). Then the activated carbons of this work could have an appreciable adsorption capacity.

3.2. Comparative study of the different adsorptions

Being clear that the acidic chemical activation by $ZnCl₂$ is preferable to that by NaOH, we made a comparative study of the two adsorbents activated by Lewis acid ZnCl₂ i.e. Ca-Sa ZnCl₂ and Ca-Av ZnCl₂.

Considering also Q_{max} we can deduce that the adsorption by CA-Sa ZnCl₂ would be more interesting than that with CA-Av ZnCl2. Although their specific surface are closed the composition and the adsorption capacity of the two adsorbents are different. Internal adsorption mechanisms could explain this better.

However, we have found that our coals are effective at low concentrations. This type of isotherm is generally characteristic of microporous activated carbon (Sun and Meunier, 2003).

3.3. Monitoring of parameters influencing adsorption

3.3.1. Influence of pH

Figure 2 shows the adsorption rate of Cr (VI) as a function of pH. The pH is an important factor in any adsorption study, since it can influence both the structure of the adsorbent and the adsorbate as well as the adsorption mechanism. It is important to know the adsorption efficiency at different pH (Barka, 2011).

Figure 2: Chromium (VI) adsorption rate as a function of pH

The maximum of adsorption is reached at $pH = 2.48$ for all the charcoals studied. Some studies by Mohan et al. (2006) and Zhang et al. (2010) showed that the adsorption of chromium (VI) by activated carbon is favorable for acidic pH values. The maximum adsorption at pH 2.48 can also be explained by the studies of Mohan and Pittman

 (2007) which reveal that; in an acid medium, the dominant ion in solution $(HCrO₄)$ reacts with the activated carbon to give Cr^{3+} at pH < 3. Neutralization of the negative charges on the surface of the carbon is favored by the supply of hydrogen ions and certainly Cr (III) ions; which would explain the high elimination of chromium in solution.

3.3.2. Influence of the adsorbent mass on the percentage of adsorption

Figure 3 shows the adsorption rate of chromium (VI) as a function of the different masses of activated carbons.

Figure 3: Chromium (VI) adsorption rate as a function of the masses of the adsorbents.

It appears from Figure 3 that the absorption rate increases with the change in the mass of adsorbent and stabilizes between 5 and 5.48 g for CA-Sa NaOH carbon. The adsorption ranges from 66.86 to 82.92 % for CA-Sa carbon (NaOH). This study reveals that activated carbon based on soda has a lower adsorption capacity than those activated with ZnCl₂. This elimination of chromium in solution by the two acid charcoals can be explained by the strong interaction between the particles of carbon CA-Sa ZnCl₂ and CA-Av ZnCl₂ causing a strong elimination of the metal cation on the surface of our acid charcoals (Manohar et al., 2002). However, this observation justifies the availability of adsorption sites on the surface of our different charcoals and the formation of the bearing marks the saturation of the adsorption sites.

3.3.3. Effect of the initial chromium (VI) concentration on the percentage of adsorption

The evolution of the adsorption percentage as a function of the initial chromium (VI) concentration is presented in Figure 4. This figure shows that the rate of chromium (VI) adsorption increases with the concentration. This indicates a gradual saturation of the adsorption sites. The saturation of the adsorption sites is done gradually until reaching a saturation level. The percentage of the maximum amount adsorbed is reached at 99.28 % for CA-Sa $ZnCl₂$, 99 % for CA Av ZnCl₂ carbon and of the order of 82 % for CA-Sa NaOH carbon. This result can be explained by the fact that the higher the concentration of the solution, the more the chromium (VI) molecules are numerous in the solution, the more they are in contact with the adsorbent then the percentage of adsorption increases. The results obtained indicate a high retention of molecules which diffuse on the surface of the particle sites (Zheng et al., 2010).

Figure 4: Chromium (VI) adsorption rate as a function of the initial concentration of the solution

3.3.4. Effect of contact time on the adsorption of chromium (VI)

The adsorption kinetics determine the contact time taken to reach the adsorption equilibrium. This is an important step in any adsorption study. Figure 5 shows the kinetics of chromium (VI) adsorption by different activated carbons.

Figure 5: Chromium (VI) adsorption rate as a function of contact time.

The curve shows that the adsorption process of chromium (VI) on the different activated carbon breaks down into two phases:

- A very fast phase where adsorption is almost complete after 75 minutes;
- A phase where adsorption almost no longer exists, the curve is almost parallel to the time axis. Equilibrium is reached in 75 minutes of contact time but the absorption rate is better with those activated with $ZnCl₂$ (with a saturation reached at 99 %) compared to the one activated with NaOH, which stabilizes at 82 %. Generally, the equilibrium time depends on the adsorbent and the adsorbate. The stabilization observed in the following minutes could be due to saturation of the adsorption sites or to one of the diffusion factors (Banat et al.,

2000). It varies from a few minutes to a few days and also depends on the anion associated with the cation to be adsorbed (Schlegel et al., 2001).

4. CONCLUSION

This work is a contribution to the research carried out in in the domain of making activated carbon from local biomass for the treatment of wastewater. Indeed, the results obtained indicate that the best activated carbons prepared from safou and avocado seeds have a specific surface of 2.903 m^2g^{-1} and 2.013 m^2g^{-1} respectively. The adsorption isotherms revealed a microporous texture with the presence of the mesopores for the two charcoals prepared. This study indicate that the adsorption rates of chromium (VI) increase appreciably with the increase in the mass of activated carbon. The pH of the solution has a considerable effect on the adsorption capacity and the pH value found optimum for the adsorption of chromium is equal to 2.48. The results of the kinetic study show the applicability of a pseudo second order kinetics model.

5. DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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