RESEARCH ARTICLE

REMOVAL OF CUPRIC IONS IN AQUEOUS SOLUTION BY ADSORPTION ON BARKS OF DACYRODES EDULIS AND MANGIFERA INDICA.

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Abstract
The adsorption of the cupric ions on bark of dacryodes edulis and mangifera indica was studied under various experimental conditions with an aqueous solution of concentration 63.55 mg/L. The effect of adsorbent dosage, the contact time and the pH of solution was examined. In all cases, the percentage of adsorbed metal increases with the contact time and the adsorbent dosage; it takes two hours of contact time to reach equilibrium with the bark of mangifera indica, whereas one needs of them three hours for those of dacryodes edulis.

On the other hand, the effect of pH on the percentage of adsorbed metal is not the same in both cases since the maximum adsorption on the bark of mangifera indica is located between pH 5 and 6, whereas with the bark of dacryodes edulis, the pH is higher than 6.

The results obtained showed that the bark of mangifera indica adsorbed the quantities of copper larger than those of dacryodes edulis; the maximum adsorption capacity determined by the interpretation of the model of Langmuir isotherms are 5.85 mg/g for the bark of mangifera indica, and 5.22 mg/g for those of dacryodes eludis.

Introduction:
Industrial development caused these last years the increase in the quantities of the liquid effluents charged in heavy metals in many countries which it is necessary to reject into the receiving medium. If these effluents are not treated before their rejection, they can generate the disappearance of certain plants and animals species (Mounia et al., 2012 ; Patil et al., 2012).

Several methods of elimination of heavy metals in aqueous solution are developed with costs and outputs various according to the nature of the pollutant to eliminate. The most used methods are chemical precipitation, solvent extraction, electrolysis and adsorption (Azzoug et al., 2010 ; Rengaraj et al., 2002).

These last years, the adsorption of the inorganic pollutants is the object of several studies; the activated carbon is the adsorbent one more used but it is too expensive (Rahangdale et al., 2017; Mahmoud et al., 2014). In recent years, many studies have been carried out using the natural adsorbents less expensive and largely available in the developing countries like the wood barks, the algae, the sugarcane bagasse (Mohammed et al., 2016 ; Nidhi Jain 2015 ; Ali Mcheik et al., 2016).

1418
However, the use of the natural adsorbents is not yet well optimized on a large scale for various reasons among which, the diversity of vegetable material and need for treating them chemically to increase their adsorption capacity (Montes et al., 2003; Prapti et al., 2015). The adsorption of the ions in aqueous solution brings into play reactions of different nature, but several authors are of agreement on the fact that the most important are the reactions of ion exchange and complexion (Meral et al., 2012). The adsorption of the ions is influenced by several parameters among which pH, the contact time, the adsorbent dosage, the initial concentration of the pollutant and the temperature (Naveen et al., 2014; Ruiti et al., 2015). The modeling of adsorption equilibrium is based the isotherms of adsorption which translate the relations between the quantity of adsorbed metal and that remained in solution. Several models of the isotherms are used but within the frame of this work, only the model of Langmuir was used to determine the maximum adsorption capacity (Mohamed et al., 2011; Omran and Mostafa 2015).

This work is a comparative study of the elimination of the cupric ions in aqueous solution by adsorption on barks of mangifera indica and dacyodes edulis which are fruit trees that one abundantly finds in Brazzaville, Republic of CONGO.

Materials and methods:

The barks of mangifera indica and dacyodes edulis were collected from trees in a district of Brazzaville in Republic of CONGO. These barks were washed with the tap water and dried in sunlight during three weeks, then dried in an oven with 105°C during three hours before being crushed and filtered until a granulometry of 75μm.

Before their use as adsorbent, they were washed with the distilled water at a quantity of 50 g in 2 liters under agitation during three hours in order to eliminate the residues of crushing and the organic compounds likely to color the solution and to disturb the determination of cupric ions using spectrophotometric method (Bandela et al., 2016).

The stock solution containing the cupric ions was prepared by dissolving a given quantity of Cu(NO₃)₂, 6H₂O in distilled water and the desired solution with the concentration of 63.55 mg/L was obtained by dilution.

The contact of the adsorbent with the solution of cupric ions was carried out in beakers of 100 ml containing 50 ml of cupric ions under agitation and various experimental conditions: After separation of the mixture adsorbent / solution by filtration, the cupric ions were analyzed with a spectrophotometer Aqualytic AL 800, with the wavelength of 800 nm by using the method of the calibration curve (Nassima and Moussa, 2010).

The equilibrium adsorption capacity qₑ (mg/g) was determined by the following relation:

\[
q_e = \frac{(C_i-C_e)V}{m}
\]

With:

- m: mass of the adsorbent in grams
- C_i: initial concentration of the ion in mg/L
- C_e: equilibrium concentration of the ion in mg/L
- V: volume of the solution in liters

The percentage of adsorbed metal is calculated by the following relation:

\[
\% \text{ adsorbed Metal} = \frac{(C_i-C_e)100}{C_i}
\]

The parameters studied during this study are the pH, the contact time and the adsorbent dosage. The pH of the solution was adjusted either with a solution of HCl 0.1 mol/L, or with those of NaOH 0.1 mol/L (Bhat et al., 2013).

The Langmuir model of the isotherms was used to determine the maximum adsorption capacity using the linear relation (Malavizhi et al., 2013).

\[
\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}C_e b}
\]

with:

- qₑ: equilibrium adsorption capacity (mg/g)
- q_max: maximum adsorption capacity (mg/g)
Ce: equilibrium concentration (mg/L)

b: Langmuir constant (L/mg)

The intercept of the curve expressing the variations of \( \frac{1}{q_e} \) as function of \( \frac{1}{Ce} \) makes it possible to determine \( q_{\text{max}} \), and the slope makes it possible to determine the Langmuir equilibrium constant \( b \).

The separation factor
\[
R_L = \frac{1}{1 + \frac{bC_i}{1}}
\]
was used to know if adsorption is favorable or unfavorable (Ackacha and Meftah, 2014).

**Results and discussion:**

**Influence of the adsorbent dosage on the percentage of adsorption:**

The percentage of the adsorbed metal as function of the adsorbent dosage is represented by the figure 1.

![Figure 1](image)

**Figure 1:** Influence of the adsorbent dosage on the percentage of the adsorbed metal

This curve shows that the percentage of adsorbed metal increases with the adsorbent dosage much more with the barks of *mangifera indica* than with those of *dacroydes edulis*. The adsorbent dosage necessary to reach equilibrium is about 15 grams in a liter of solution of cupric ions for the two adsorbents.

This increase in the percentage of the adsorbed metal with the adsorbent dosage can be explained by an increase of active surface and thus amongst sites of adsorption (Abdellaoui et al., 2014).

Indeed, an increase in the adsorbent dosage involves that amongst sites of adsorption; but as is held the phenomenon of adsorption, the occupation of the first sites of adsorption makes increasingly difficult the adsorption of the ions and that involves a reduction the reaction speed of adsorption which results in the existence of a stage on the curve (Torab-Mostaedi et al., 2010).

**Influence of the contact time on the percentage of adsorbed metal:**

The adsorption of metal in aqueous solution depends on the contact time. The Figure 2 represents the variations of the percentage of the adsorbed metal on each adsorbent as function of the contact time.
Figure 2: Influence of the contact time on the percentage of adsorbed metal

This curve shows that in each case, the speed is fast at the beginning and decrease with time. It takes two hours of contact time to reach the equilibrium of adsorption with the barks of *mangifera indica* whereas one needs of them three hours with the barks of *dacrodes edulis*. When equilibrium is reached, the percentage of the adsorbed metal on the barks of *mangifera indica* is higher than that obtained on the barks of *dacrodes edulis*. This difference can be explained amongst other things by the chemical composition and properties which are not the same for the two adsorbents, in particular the number of adsorption sites and specific surface.

Influence of the pH on the percentage of adsorption:

The effect of the pH was studied in the interval from 2 to 6 for a contact time of two hours; the maximum value of the pH equal to 6 was retained to avoid the precipitation of the cupric ions which would be likely to cause an interaction between the phenomena of adsorption and precipitation of Cu(OH)$_2$ (Ackacha and Meftah, 2014).

The figure 3 shows the variations of the percentage of the adsorbed metal as function of the pH of the solution for each adsorbent.

Figure 3: Influence of the pH on the percentage of adsorption of metal

This figure shows that the percentage of adsorbed metal increases with the pH to reach a maximum between pH 5 and 6 on the barks of *mangifera indica*. Similar results were already announced by other authors. At the time of a study of the adsorption of the cupric ions on Ferrocene, Qian et al., (2013) obtained similar variations...
to those which we obtained on \textit{mangifera indica} and these authors explain the variation by interactions between the species Cu$^{2+}$, Cu(OH)$^+$ and the functional groups present at the surface of the adsorbent. In addition, Ksakas et al., (2015) studied the adsorption of the ions Cr (VI) on vegetable materials and allocated this variation by the existence of the electrostatic forces between the surface of the adsorbent and the various species charged with chromium present in the solution according to the pH. Indeed, according to the pH of the solution, the particles of the adsorbent can be charged negatively or positively so as to have effects on the electrostatic attraction forces between the ion and the adsorbent (Kumar et al.,2014). On the other hand, this percentage does not pass by a maximum with the barks of \textit{dacroydes edulis}.

We think that this difference in behavior of the Cu$^{2+}$ ions on the two adsorbents can be explained by the fact that they do not have the same surface properties.

**Determination of the maximum adsorption capacity**: -

The determination of the maximum adsorption capacity was carried out by exploiting the linear relation of the Langmuir isotherm. Figure 4 represents the variations of $1/q_e$ as function of $1/C_e$ obtained during the adsorption of the cupric ions on the barks of \textit{mangifera indica}.

![Figure 4: Langmuir Isotherms for adsorption of cupric ions on mangifera indica](image)

This curve gives the intercept equal to 0.1711 and a slope equal to 0.5842 which made it possible respectively to determine the maximum adsorption capacity $q_{\text{max}} = 5.85$ mg/g and the Langmuir equilibrium constant $b = 0.29$ L/mg.

The figure 5 represents the variations of $1/q_e$ as function of $1/C_e$ obtained during the adsorption of the cupric ions on the barks of \textit{dacroydes edulis}. 

![Figure 5: Variations of $1/q_e$ as function of $1/C_e$](image)
In the same way, the maximum adsorption capacity on *dacroydes edulis* is \( q_{\text{max}} = 5.22 \text{ mg/g} \) and the constant of equilibrium of Langmuir \( b = 0.06 \text{ L/mg} \).

The comparison of the maximum adsorption capacities shows that the barks of *mangifera indica* adsorb more cupric ions in aqueous solution although the difference is not important. Compared with the results of the literature, these two adsorbents do not adsorb great quantities of cupric ions. For example, Ragwan et al. (2016) obtained maximum adsorption capacity of the cupric ions in aqueous solution on the powder of palm nuts of 76.2 mg/g.

All parameters determined by the exploitation of the model of Langmuir isotherms are given in the table I.

| Parameters       | Mangifera indica | Dacroydes edulis |
|------------------|-------------------|------------------|
| \( q_{\text{max}} \text{(mg/g)} \) | 5.85              | 5.22             |
| \( b \text{(L/mg)} \)     | 0.29              | 0.06             |
| \( R^2 \)              | 0.9882            | 0.9761           |

The separation factor \( R_L \) have values equal to 0.05 and 0.20 respectively for adsorption on the barks of *mangifera indica* and *dacroydes edulis*; these values higher than zero indicate that the adsorption of the cupric ions on these two adsorbents is favorable.

**Conclusion:**

The objective of this work was to study the possibility of eliminating the cupric ions in aqueous solution by adsorption on barks of *mangifera indica* and *dacroydes edulis*. The results obtained showed that these two adsorbents can be used to adsorb cupric ions in aqueous solution, although the eliminated quantities are not too large when one them compared to other adsorbents. The percentage of adsorbed metal is function of pH; contact time and adsorbent dosage. In both cases, the contact time between the solution and the adsorbent to reach equilibrium is two to three hours according to the adsorbent whereas the best percentage of adsorption is obtained between pH 5 and 6. The percentage of absorbed metal is higher on the barks of *mangifera indica* compared to those of *dacroydes edulis*.

The determination of the maximum adsorption capacities by the exploitation of the Langmuir isotherms gave 5.85 and 5.22 mg/g respectively on the barks of *mangifera indica* and *dacroydes edulis*.

The value of the separation factor higher than zero in both cases indicated that the adsorption of the cupric ions is favorable on these two adsorbents.
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