



Adsorption of Copper(II) and Chromium(VI) Metal Ions from Aqueous Solution using Barks of *Moringa oleifera lam.* as Adsorbent

Tchoumou M.*, OSSEBI J.G., Bitalika Malongo C.P. and Mananga C.G

Laboratory of Applied Inorganic Chemistry, Faculty of Sciences and Technology, Marien Ngouabi University, P.O. Box 69 Brazzaville, CONGO

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Abstract

The removal of copper(II) and chromium(VI) metal ions from aqueous solution was studied by the technique of adsorption on the barks of *moringa oleifera*, under various experimental conditions. The effect of some parameters as pH of solution, contact time and adsorbent mass were examined. The results obtained showed that the quantity of each adsorbed metal increases with contact time and adsorbent mass. To obtain a high quantity of adsorbed metal, the pH of the solution was 5 for each ion, the contact time was two hours for copper(II) ion and four hours for chromium(VI) ion, and the adsorbent mass was 16 g/L for each ion. Under optimal conditions, it was found that the amount of removal metal was 91.53% for copper(II) and 90% for chromium(VI) ions. The models of Langmuir and Freundlich isotherms were used to determine the different equilibrium parameters for the distribution of metal ion between solution and adsorbent. The value found for Langmuir constants were respectively 0,14 L/mg for copper(II) ion and 0,36 L/mg for chromium(VI) ion, whereas the Freundlich constants were respectively 0,5 L/mg for copper(II) ion and 0,34 L/mg for chromium(VI) ion. The determination of maximum adsorption capacity by using the Langmuir isotherm gave a value of 3,10 mg/g for copper(II) ion and 1,39 mg/g for chromium(VI) ion, showed that adsorption followed the order $Cu(II) > Cr(VI)$.

Keywords: Adsorption, bark, isotherm adsorption, maximum adsorption capacity, moringa oleifera.

Introduction

The agricultural and industrial activities generate great quantities of heavy metals in waste waters with high concentrations which require their elimination before the rejection in the natural environment to avoid many damage¹⁻³.

Several methods were developed to remove metal ions, as precipitation, ion-exchange and adsorption. The commercial activated carbon is the adsorbent more used for elimination of the ions in aqueous solution but it is very expensive⁴. In the last past years, many studies were carried out on the natural adsorbents use, less expensive and commonly available in the developing countries which abound in large forests⁵⁻⁸. The different parts of *Moringa oleifera* were used in the medical fields, but in the literature, some research tasks on the ability of the seed of this plant to clarify the water^{9,10}. This study is a contribution on investigation of adsorbent properties of the barks of *Moringa oleifera* to remove copper(II) and chromium(VI) ions in aqueous solution. The adsorption of the metal ions in aqueous solution is a process which utilizes several types of reactions; many researchers agree that the ion exchange intervenes in the majority of the cases^{11,12}. In this process, the metal ion is distributed between the solution and the adsorbent; the study of this equilibrium distribution is carried out by using the models of adsorption isotherms which give the relation between the quantity of the ion in the solution and its adsorbed quantity^{13,14}. Several models of isotherms were proposed to describe the equilibrium distribution of the ions, but

within the framework of this work, only the models of Langmuir and Freundlich were exploited¹⁵.

The model of Langmuir isotherm considers that during the process, the adsorption equilibrium is established until the formation of monolayer with identical sites and that the particles adsorbed assume no interaction between them^{16,17}. The Linear Langmuir equation is given by Equation -1

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max} C_e b} \quad (1)$$

In this equation, q_e is the adsorption capacity (mg/g), q_{max} is the maximum adsorption capacity (mg/g), b is the Langmuir equilibrium constant (L/mg) and C_e the equilibrium concentration (mg/L). The model of Freundlich isotherm is applied to the solids presenting several adsorption sites, and having a heterogeneous surface, followed by interaction between adsorbed metal¹⁸⁻²⁰. The linear Freundlich equation is given by the equation - 2

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

In this equation, K_F is the Freundlich equilibrium constant, and n the adsorption intensity.

When $n = 1$, all sites become similar and the isotherm of Freundlich is brought back to that of Langmuir.

Material and Methods

Preparation of the barks used as adsorbent: For this study, the barks of *Moringa oleifera* used were collected in a locality of Brazzaville, Republic of CONGO. The barks were dried under normal sunlight conditions during two weeks before being used as adsorbent of copper(II) and chromium(VI) ions from aqueous solution.

The barks were crushed and sifted to obtain the particles of dimensions lower than 100 μm , then washed with distilled water during two hours to remove all particles adhering on the surface of adsorbent, the soluble impurities and the organic compounds with can color the solution and perturb the spectrophotometric determination of the metal ion before and after adsorption experiments. The adsorbent was then dried at 70°C during four hours in a dryer²¹.

The figure-1 shows the powder of barks of *Moringa Oleifera* used as adsorbent of copper(II) and chromium(VI) ions.

Preparation of the solution of metal ions: The stock of aqueous solution of each metal ion of concentration 10⁻² mole/L was prepared with laboratory reagent as Cu(NO₃)₂.3H₂O for copper(II) ion and K₂CrO₄ for chromium(VI) ion.

By dilution of this solution with distilled water, the working solution of concentration 10⁻⁴ mole/L for each metal ion was prepared.

Adsorption experiments: The adsorption experiments of copper(II) and chromium(VI) ions were carried out with solutions of initial concentration C₀, respectively equal to 6.34 mg/L and 11.75mg/L.

For each experiment, a volume of 50 ml of solution of metal ion was mixed with a given mass of adsorbent at defined pH in a beaker of 100 ml; the mixture was then agitated during a given time. After agitation, the solution and the adsorbent were separated by filtration on filter paper. To determine the equilibrium concentration C_e of each metal ion after the adsorption experiments, the resulting solution were analyzed by UV visible spectrophotometry at the wavelength corresponding to the maximum absorption of each ion, 800 nm for the copper(II) ion et 360 nm for the chromium(VI) ion, by using the method of the calibration curve. The principal parameters studied are the contact time, the pH of solution and the adsorbent mass. The contact time varied between 0.5 and 5 hours, the adsorbent mass between 0.2 and 1.2 g, whereas the pH of solution varied from 1 to 6; the aqueous solution of HCl 0.1 mole/L or NaOH 0.1 mole/L was used to adjust the pH of each solution at the desired value²².

The percentage of adsorbed metal was determined by the equation -3.

$$\%Ads = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (3)$$

The determination of different equilibrium parameters for the adsorption of each metal ion was carried out by using the models of Langmuir and Freundlich isotherms.

The plot 1/q_e = f(1/C_e) of Langmuir isotherm was used to determine the maximum adsorption capacity q_{max} and the equilibrium constant b for each metal ion.

The plot lnq_e = f(lnC_e) was used to determine the Freundlich equilibrium constant K_F and the intensity of adsorption n.



Figure-1

Powder of barks of *Moringa oleifera* used as adsorbent of copper(II) and chromium(VI) ions

Results and Discussion

Influence of contact time: The influence of contact time on the adsorption capacity of copper(II) and chromium(VI) ions was studied with a solution of initial concentration 6.34 mg/L and 11.75 mg/L respectively ; the aqueous solution of NaOH 0,1 mol/L was used to adjust the pH of solution to 5 , the adsorbent mass was 1 g in 50 ml of solution and the contact time was two hours. The figure-2 below represents the variation of the percentage of each adsorbed metal as function of contact time.

This figure-2 shows that the quantity of each adsorbed metal increases with the contact time; the maximum of adsorption intervenes after two hours for the copper (II) ion, and after four hours for the chromium(VI) ion. The shape of this curve indicates that two stages intervene during the adsorption process: a fast stage between zero and one hour, followed by a slow stage between one and five hours. To explain this phenomenon, Mohamed indicated that this trend of adsorption can be assigned to the nature of the adsorbent and the number of available adsorption sites to the surface of the adsorbent which affect the time necessary to reach the equilibrium of distribution of the ion between the solution and the adsorbent²³. In its work, Hefne announced that at the beginning of adsorption process, there exist a large number of adsorption sites on the surface of the adsorbent, and that as the metal ion gradually occupy the adsorption sites on the surface of material, the resistance of transfer of matter inside the particles of the adsorbent increases and adsorption of metal becomes increasingly difficult²⁴.

Influence of the pH of solution: The pH of solution influences considerably the process of adsorption of the ions of heavy

metals in aqueous solution. It's effect on adsorption of the copper(II) and chromium(VI) ions was studied from a solution of initial concentration of 6.34 mg/L for the copper(II) ion and 11.75 mg/L for the chromium(VI) ion with the adsorbent mass of 0.8 g in 50 ml of solution, during two hours. The variation of the pH of each solution in the interval from 1 to 6 was obtained by adjusting the value by addition of HCl 0.1 mole/L or NaOH 0.1mole/L. A pH-meter HANNA Instrument HI 8341 with a combined glass electrode was used to measure the pH of each solution. The figure-3 below represents the variation of the percentage of each adsorbed metal as function of the pH.

As be seen in this figure-3, the adsorption capacity of each ion is affected by the pH of solution. Many authors are indicated that the variation of the pH of solution modifies the properties of surface of the adsorbent and bring about the variation of the adsorption capacity because the surface charge of the adsorbent and the nature of the species of the metal ion present in the solution were modified^{25,26}. The maximum of adsorption intervenes at pH 5 for the copper (II) and chromium (VI) ion. These results confirm those already announced by other researchers who indicated that the adsorption sites are constituted of group of weak acids and that the ion exchange intervenes in the process of adsorption²⁷.

Influence the adsorbent mass: To study the influence of adsorbent mass on the percentage of each adsorbed metal, the concentration of copper(II) and chromium (VI) ions in the aqueous solution were respectively 6.34 and 11.75 mg/L; for each ion, the adsorbent mass varied from 0.2 to 1.2 g in 50 ml of solution, the pH of each solution was adjusted to 5 with NaOH 0.1mol/L, and the contact time was two hours.

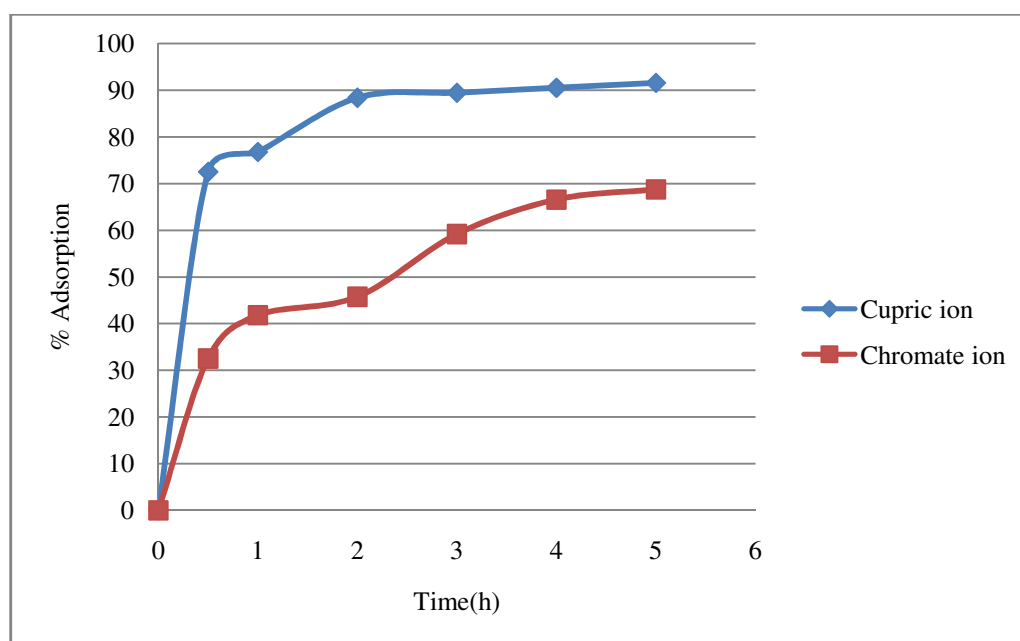


Figure-2
Influence of contact time on the percentage of adsorbed metal

The figure-4 here represents the variation of the percentage of each adsorbed metal as function of the adsorbent mass.

percentage of each adsorbed metal tends to be stabilized with the appearance of a stage of saturation of the process.

According to figure-4, the quantity of each adsorbed metal increases with the adsorbent mass. This result is agreement with those of Onundi *et al* which explains this phenomenon by the increase of amount of active sites on the surface of the adsorbent²⁸. With a solution containing 0.8 g of adsorbent, the

Determination of the Langmuir and Freundlich parameters:
 The determination of the different equilibrium parameters q_{max} , b , K_F and n was carried out by interpretation of linear equation of the models of Langmuir and Freundlich isotherms.

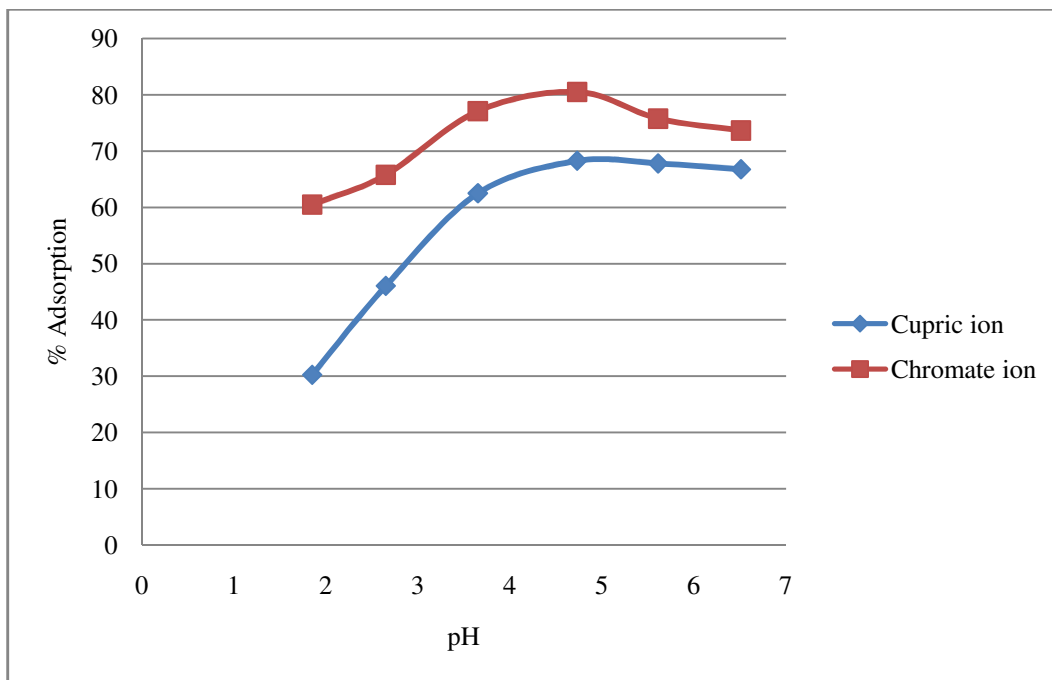


Figure-3
 Influence of pH on the adsorbed metal

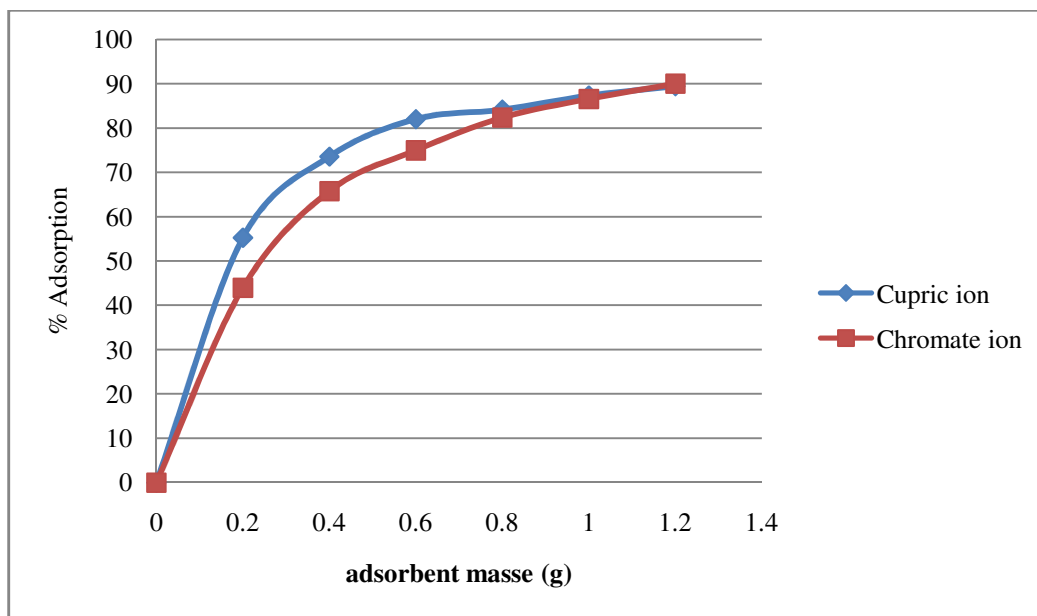


Figure-4
 Influence adsorbent mass on adsorbed metal

The figures-5 and 6 represent the curves $1/q_e = f(1/C_e)$ of the Langmuir isotherm of each metal ion which allow to determine the maximum adsorption capacity q_{max} from the intercept, and the Langmuir equilibrium constant b from the slope of line.

Freundlich isotherm of copper(II) and chromium(VI) ions used to determine, K_F and n parameters.

The values of different parameters found using the models of Langmuir and Freundlich isotherms adsorption are given in the table-1.

The figures-7 and 8 represent the curve $\ln q_e = f(\ln C_e)$ of

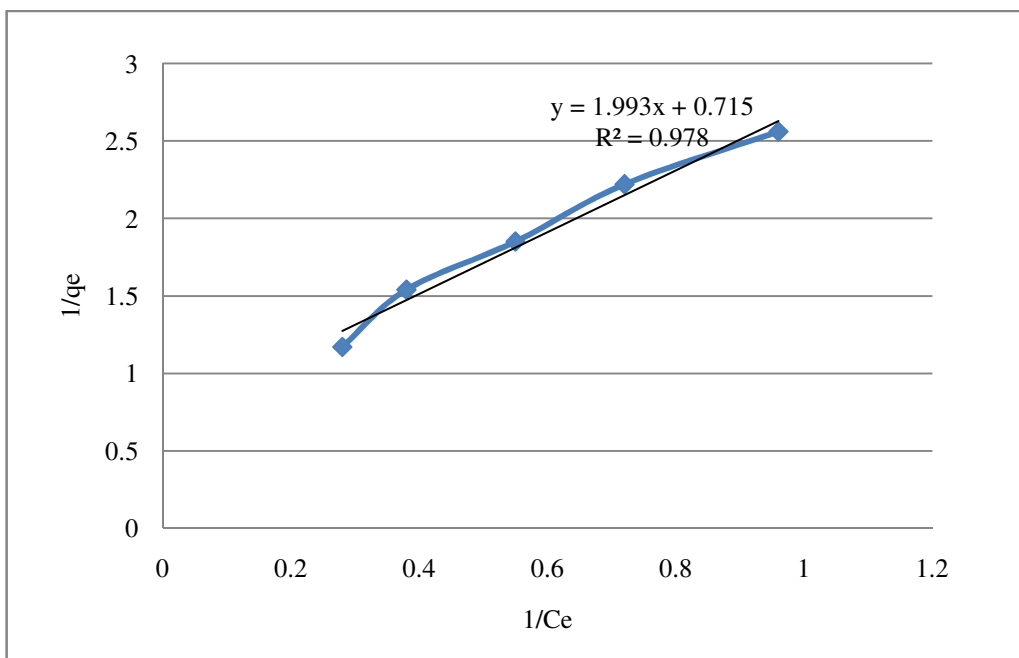


Figure-5
 Langmuir adsorption isotherm of chromium(VI) ions

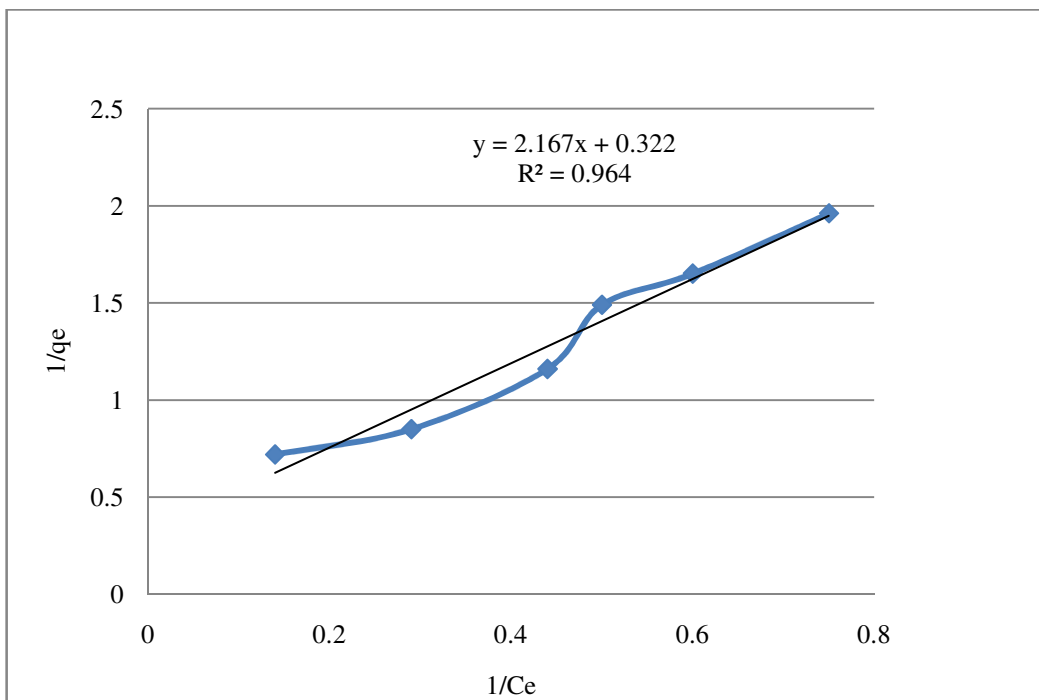


Figure-6
 Langmuir adsorption isotherm of copper(II) ions

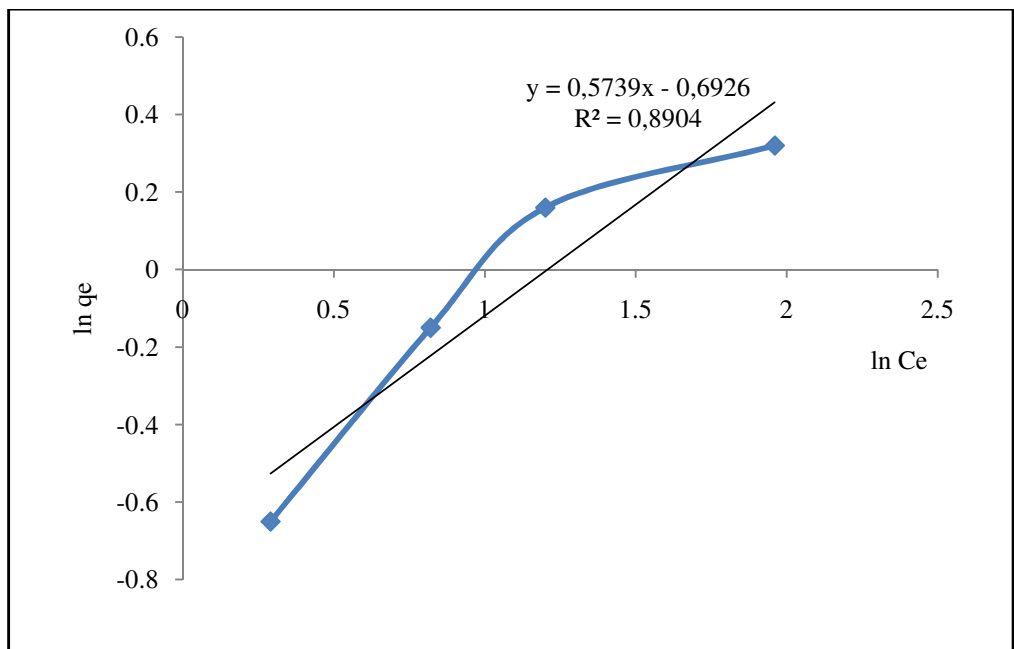


Figure-7
 Freundlich adsorption isotherm of copper(II) ions

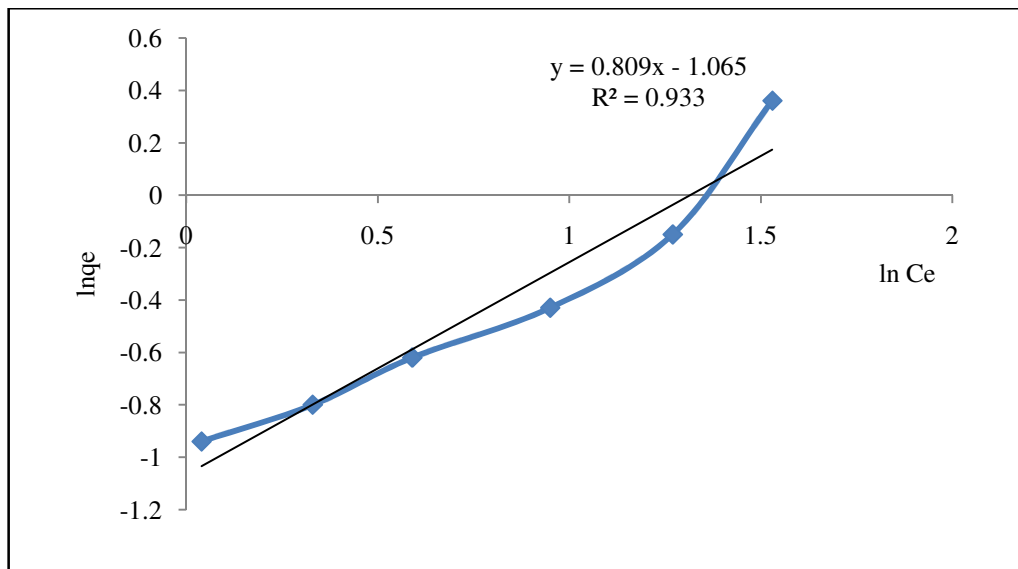


Figure-8
 Freundlich adsorption isotherm of chromium(VI) ions

Table-1
 Langmuir and Freundlich parameter of cupric and chromate ions

Ions	Langmuir parameters			Freundlich parameters		
	q_{max} (mg/g)	b (L/mg)	R^2	K_F	n	R^2
Copper (II)	3.1	0.14	0.99	0.5	1.74	0.89
Chromium(VI)	1.39	0.36	0.978	0.34	1.23	0.834

The high value of R^2 for each metal ion in this table indicated that the data are fitted in every model. As R^2 found with the Langmuir model is superior to those of Freundlich model, we can conclude that the model of Langmuir isotherm represents best the process of adsorption of Chromium(VI) and Copper(II) ions on the barks of *Moringa Oleifera*²⁹.

Conclusion

The objective of this work was to study the adsorbent properties of the barks of *moringa oleifera* on the adsorption of the copper(II) and chromium(VI) ions from aqueous solution under various experimental conditions.

From the results obtained, it appears clearly that this adsorbent can be used to eliminate these ions from aqueous solution under the definite experimental conditions. The quantities of adsorbed metal are function of all studied parameters which are the contact time, the pH of solution and the adsorbent mass. The high adsorption capacity of each metal ion was obtained under the following experimental conditions: * for copper(II) ion : pH 5; contact time : 2 hours ; adsorbent mass : 16 g/L ; * for chromium (VI) ion: pH 5 ; contact time: 4 hours ; adsorbent mass: 16 g/L.

The application of the models of Langmuir and Freundlich isotherms to the distribution equilibrium of the metal ion between the adsorbent and the solution gave access the various constants characteristic of the process of adsorption of each ion under these experimental conditions.

The interpretation of the experimental results according to model of Langmuir isotherm gave a maximum adsorption capacity of 3.10 mg/g for the copper(II) ion, and 1.39 mg/g for the chromium(II) ion.

The comparison of these results shows that the barks of *Moringa oleifera* adsorbs the copper(II) ions best that the chromium(VI) ions under the same experimental conditions

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