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RESEARCH ARTICLE

ADSORPTION OF METHYLENE BLUE USING UNACTIVATED CORN COBS POWDER FROM ADAMAWA REGION OF CAMEROON

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ABSTRACT

The agricultural waste corn ears have been used in the depollution of sewage loaded with coloring, including Methylene Blue (MB). The adsorption balance was reached in 15min. The yield of elimination of Methylene Blue reached 96.85%. The experimental data are analyzed by two isotherms (Freundlich and Temkin). The Freundlich nf constant is between 0 and 0.5. We have studied thermodynamic parameters in the temperature range of 298K and 338K. We got free energy negative ($\Delta G<0$), the standard enthalpy of the removal positive and below 50 KJ/mol, demonstrating that the reaction is favorable, spontaneous, endothermic, and of physical nature. The kinetic model of pseudo second order and Elovich were applied is the correlation coefficients R2 is 0.99. The reactions are made according to the models of pseudo second order and Elovich suggesting the hypothesis that the mechanism of the reactions are done in two phases:

- The diffusion of the BM towards the surface of the adsorbent;
- The interaction between the adsorbate molecules (MB) and the surface of the adsorbent, suggesting the existence of chemisorption.

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INTRODUCTION

Activities, whether human or industrial, are generally a source of pollution because of multiple pollutants released into the environment. This is the case of dyes that are often used in aqueous solutions and whose environmental consequences are numerous. The massive rejection of toxic residues in the natural environment led to the appearance of numerous risks for the balance of the natural environment and ecosystems, but also for human health. This has stimulated the improvement of existing depollution techniques and the development of new pollution control. Various depollution techniques have been used for the removal of certain pollutants soluble in industrial or domestic effluents. This is the case of electrolysis, the flotation, precipitation, ion exchange, liquid-liquid extraction, filtration membrane. However, these processes are expensive and lead to the generation of large amounts of sludge or drift (Robinson *et al.,* 2001). Adsorption is one of the most adopted techniques for this removal of pollutants, because of its great ability to purify contaminated water. Activated carbon is the most commonly used adsorbent but remains very expensive and also requires regeneration constituting a limiting factor. This has therefore encouraged research by orienting them towards treatment processes using less costly and widely available natural materials such as clay (Adjia *et al.,* 2014), corncobs (El-Hendawy *et al.,* 2001, Cao *et al.,* 2006), eggshells (Khelifi *et al.,* 2016), palm waste (Hazourli *et al.,* 2007). Few studies in our opinion have used corncobs in the depollution of wastewater. The present study consists in testing Ngaoundere-Cameroun corncobs in the depollution of water loaded with organic pollutants such as Methylene Blue. To this end, we have prepared a synthetic solution of Methylene Blue in the laboratory and carry out the clean-up tests to follow the behavior of this new material in the elimination of this pollutant.

MATERIALS AND METHODS

Preparation of the bioadsorbent: The corn cobs are collected locally in maize fields at Ngaoundere Cameroon, dried and then crushed and sieved to obtain the powder of corncobs smaller than 300μm, washed with distilled water and dried in an oven at 105 ° C put in soda base 0,1 N for 24 hours. Corn cobs powder and soda where used in proportion of 1/5 (weight of corn cobs powder/volume of soda) (Khormaei *et al.,* 2007) In this way, the base activated corn cobs powder (BACCP) is obtained ready for use.

Preparation of the mother solution of Methylene Blue: Weigh 1000 mg of solid Methylene Blue, dissolve it in 1 liter of distilled water to obtain the 1000 mg / L concentration solution.

Adsorption in batch mode: The adsorption in batch mode was done using a magnetic stirrer at a constante rate of 250tr /min on which was deposited a 250 ml beaker containing our BM solution of concentration 10 mg / L at a volume of 20 ml in which, 100mg corncobs powder was added for predefined times. The corncobs powder is separated from the solution using watmann filter paper and the optical density is read from a SCHIMATZU brand spectrophotometer to determine the residual concentration using the calibration line.

RESULTS AND DISCUSSION

The influence of the contact time: We did the contact time study using the initial concentration of 10mg / L, a volume of 20mL and a corncobs powder mass of 100mg. In case, the pH of the solution remained natural without adjustment. The result of this experiment is given in Figure 1 below. The contact time needed to reach the set balance is 25min. The experience has shown that there is no change after these 25min.

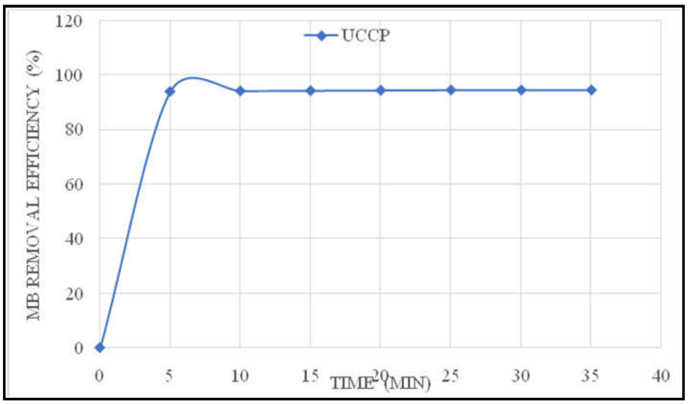


Figure 1. The influence of contact time on the adsorption of MB by UCCP

Influence of the mass of the adsorbent: We did the study of the dose of adsorbent's influence using the initial concentration of 10mg / L, a volume of 20mL and varied the mass of corncob powder from 100mg to 600mg per step of 100mg by keeping the pH of the natural solution without adjustment. The result of this experiment is given in Figure 2 below.

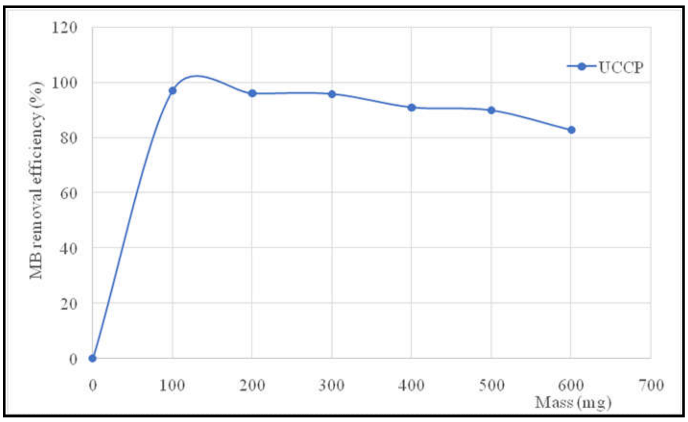


Figure 2. Influence of mass on MB adsorption by UCCP

The adsorption is maximum at the mass of 100mg which in the continuation of the work is considered as being the optimal mass and that the efficiency of the elimination decreases when the mass of the adsorbant increases, this same tendency is also observed in the works of (Mira *et al.,* 2016) when they eliminated Methylene Blue by three types of non-activated eucalyptus powder of different grain size. This behavior can be explained by the fact that: As long as the amount of adsorbent added to the dye solution is low, the dye cations can easily access the adsorption sites. The addition of adsorbent makes it possible to increase the number of adsorption sites, but the dye cations have more difficulty in approaching these sites because of the bulk. A large amount of adsorbent creates agglomerations of particles, resulting in a reduction in the total adsorption surface area and, consequently, a decrease in the amount of adsorbate per unit mass of adsorbent (Asmaa et *al.* 2010).

Influence of initial concentration: To study the influence of the initial concentration we varied the initial concentration from 10mg / L to 60mg / L in steps of 10mg / L, a volume of 20mL and a corn powder mass of 100mg keeping the pH of the natural solution without adjustment. The result of this experiment is given in Figure 3 below.

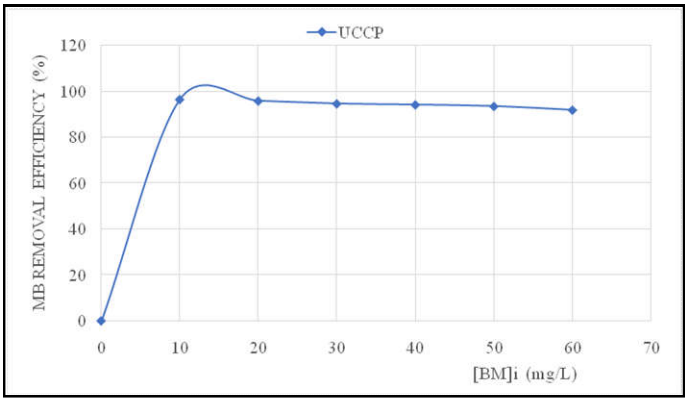


Figure 3. Influence of initial concentration

We observe that the curve has two levels: the first level when the curve increase, which results in the increasing of the efficiency of the elimination situated at the concentration less than 10 mg/L and the second step which shows a general decrease of the curve which results in the decrease of the efficiency of the elimination situated at the concentration more than 10 mg/L. We conclude that, the efficiency of the elimination follows the concentration of solution. When the pollutant concentration increases, the efficiency of the removal decreases because of the fact that, at low concentrations, the ratio of the initial number of MB to the available adsorption surface is low, therefore the removal rate becomes concentration independent, and at high concentrations saturation of the available adsorption sites is observed, and thus the adsorption becomes concentration dependent. Adsorption rates decrease when the dye concentration increases, this is an increase in competition at the adsorption sites, whereas competition decreases at active sites of the adsorbent at low concentrations (Dawood and Sen, 2012). The best performance is obtained at the concentration of 10 mg / L.

Influence of initial pH: The initial pH of the colored solutions is a very important parameter to control the adsorption process (Tavlieva *et al.,* 2013), it has an effect on the adsorbed quantity. It can change:

- The surface charge of the adsorbent ;

- The degree of ionization of the adsorbate ;
- The degree of dissociation of the functional groups of the active sites of the adsorbent (Nandi and Sunil, 2017).

To study the influence of the initial pH we used the initial concentration of 10mg / L, a volume of 20 mL and a corn cobs powder mass of 100mg by adjusting the pH of the solution from 2 to 12 using a solution of soda and sulfuric acid of normality 0,1N. The variation of the MB adsorption rate as a function of the pH is graphically represented in Figure 4 below. There is an increasing trend of the curve showing three levels. The first between pH< 2, the curve grows faster with the increase in pH, the second where 2<pH<8, the curve grows less fast with the increase in pH and the third where 8<pH<12, the growth of the curve is less sensitive with the increase in pH. The result shows that the removal efficiency increases and reaches 96.19% with pH increasing. The maximum elimination is reached at pH = 12. This increase in MB adsorption with increasing of pH is noted in the work of (Saritha *et al.,* 2015).

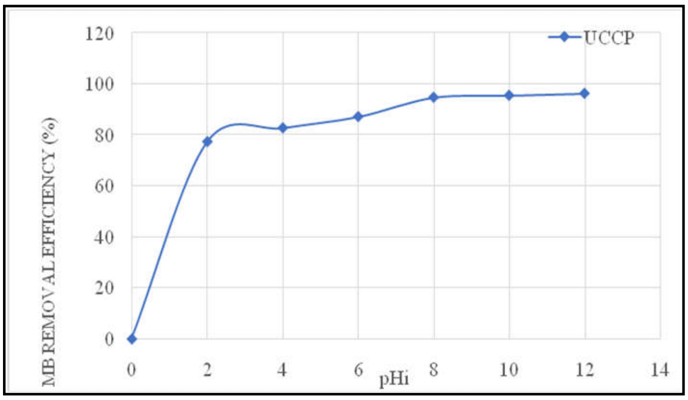


Figure 4. Influence of the initial pH on the adsorption of BM by UCCP

Influence of temperature: The influence of temperature on the adsorption of BM was studied using beakers containing 20 ml of solutions each, immersed in a thermostatically controlled water bath to preserve the desired constant temperature. The values of the temperatures studied were 25 ; 35; 45, 55 and 65° C respectively. The whole is agitated during the contact times which is 25min and the filtrate is analyzed spectrophotometrically. The result of this study is shown in Figure 5 below.

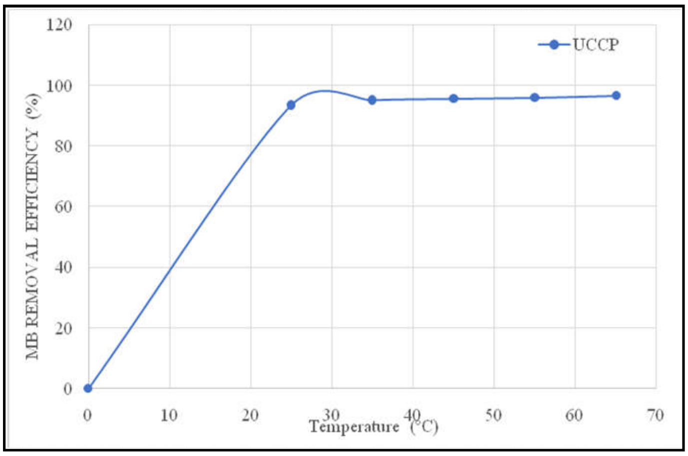


Figure 5. Influence of temperature on MB adsorption by UCCP

The observation of the figure above, allows us to see that the percentage of removal of MB by corn cobs powder increases with the increase in temperature which explains the endothermic nature of the reaction. In addition, it is observed that an increase in temperature improves the adsorption capacity of the BM by the corncobs powder. The effect of temperature on the adsorption of cationic dyes has been studied in many studies, most of them have noted a positive influence of temperature on the adsorption capacity of aluminosilicates (Doğan *et al.,* 2007). The increasing the temperature facilitates the diffusion of the adsorbed molecules to the internal pores of the adsorbent particles by decreasing the viscosity of the solution.

Adsorption isotherms

The Freundlich isotherm: The simple and empirical model of Freundlich (1909) applies to many cases, especially those of multilayer adsorption with possible interactions between adsorbed molecules (Figure 6). The linear expression of the Freundlich equation is:

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

Kf (mg $^{(1-n)}$.L^n.g^{-1}) is a constant relative to the adsorption capacity. This (mg.L^{-1}) is the concentration of MB at equilibrium and qe is the adsorption capacity (mg.g-1).

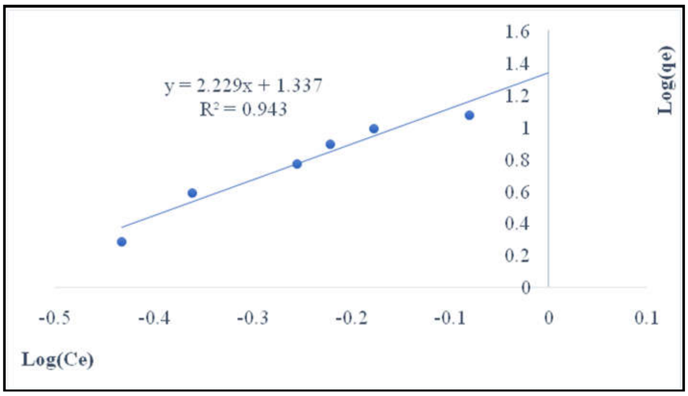


Figure 6. Isotherm of the Freundlich

Isotherm of Temkin: Temkin's (1940) model is based on the assumption that the adsorption heat due to interactions with the adsorbate decreases linearly with the rate of recovery during adsorption in the gas phase. It is an application of the Gibbs relation for adsorbents whose surface is considered to be energetically homogeneous. (Limousin *et al.,* 2007, Gimbert *et al.,* 2008) have proposed using this model in the liquid phase, (figure7) tracing qe or q according to lnCe according to the following expression:

$$\frac{q_e}{q_{mqx}} = \theta = \frac{RT}{\Delta Q}\ln(K_T.C_e) \quad (2)$$

R = 8.314 J.mol^{-1}. K^{-1}
T: Absolute temperature (inK)
ΔQ: Variation of adsorption energy (in J.mol-1)
K_T: Temkin's constant (in L.mg-1)
B_T = (qm RT) / ΔQ is the slope of the representation of the equation

$$q_e = B_T \ln A + B_T \ln X_e$$

The introduction of the value of q_m (for example from the application of Langmuir) makes it possible to calculate the variation of adsorption energy ΔQ.

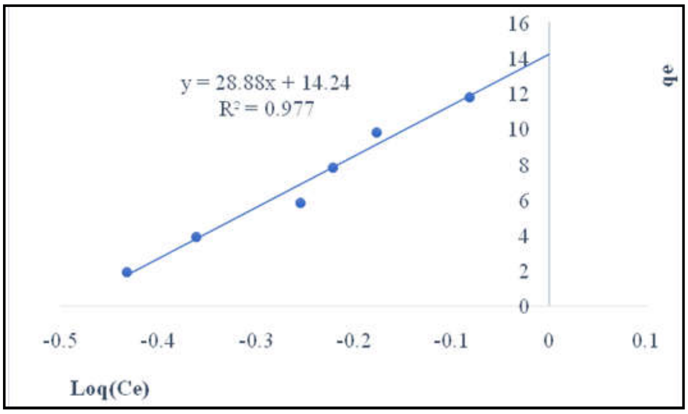


Figure 7. Isotherme de Temkin

The following table 1 gives a summary of the adsorption isotherm constants of MB by corncobs.

Table 1. Parameters of the Freundlich and Temkin adsorption isotherm

Corncobs powders	Isotherm of Freundlich			Isotherm of Temkin		
	K_F $mg^{(1-n)}.L^n.g^{-1}$	n	R^2	B	A (L/g)	R^2
UCCP	3,808	0,449	0,943	28,881	1,638	0,998

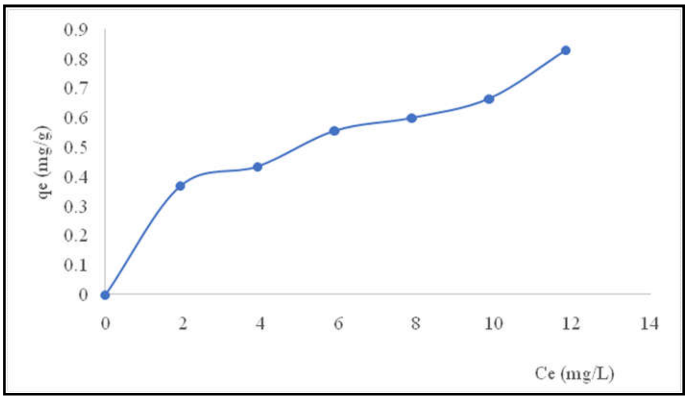
K_F = Freundlich adsorption capacity,
n = Adsorbent adsorbate affinity,
B = Temkin constant,
A = Temkin isotherm constant,
R^2 = Coefficient of determination.

According to the table 1 the Freundlich isotherm, $0 < n < 0.5$, then the reaction is favorable. $R^2 > 0.90$ therefore these isotherms allow to describe the adsorption phenomena studied with a more favorable description in the case of the Temkin isotherm since R^2 in here is greater than 0.99. In order to plot the variation of the amount of adsorbed MB per gram of adsorbent (q_e) as a function of the equilibrium concentration (Ce). BM adsorption isotherms were made by the corncob powder at the temperature of 25 °C, at normal pH of the solution without adjustment and at equilibrium time of 25 minutes using the following relationship:

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

Where:
Ci : The initial concentration of the MB solution ;
Ce : The concentration of the MB solution after adsorption ;
M : The mass of the corncob powder used;
V : The volume of the MB solution.
The modeling results obtained gives us the following figure :

This Figure 8 shows three levels. The adsorption of BM is very strong at low residual concentration (first level), which indicates a high affinity between the MB and the adsorbent. In addition, the curve shows that the adsorbed quantity rapidly increases and reaches the maximum amount of MB adsorption which is 11.834 mg / g. It should be remembered that the increase in temperature has improved the adsorption of BM by corncobs.



Figures 8. MB adsorption isotherm on unactivated cornobs (UACCP)

The curve of figure 8 is similar to the S shape, it has a point of inflection revealing at least two adsorption mechanisms. This is the case, for example, when a first layer of solute is first adsorbed and when the adsorption of one or more additional layers becomes favored. It should also be noted that when this tends towards zero, the slope of the isotherm is constant. The S forms is the form of the IUPAC classification. Our experimental results have been confronted with the theoretical models of Freundlich and Temkin. We have established the theoretical models on the basis of certain assumptions. The experimental data obtained seem to be in agreement with the hypotheses above. This allows us to assume that the assumptions made are true for the experiment conducted. This allowed us to obtain information on the adsorption mechanism.

Conclusion

The purpose of our study was to remove Methylene Blue from wastewater using a bioadsorbent obtained from native corn cobs. This study is a contribution to the water treatment sector. The study is based on the elimination of Methylene Blue contained in a synthetic solution. In order to conduct this study, we studied the influences of certain parameters such as the contact time, the influence of the dose of the adsorbent, the influence of initial concentration, the influence of the initial pH and the temperature. The study of kinetics was conducted as well as the study of thermodynamic parameters. The adsorption equilibrium was reached after 15 minutes. The experimental data are analyzed using Freunlich and Timkin isotherms. The value of Frendlich's constant nf is between 0 and 0.5, we are in a phase of favorable adsorption. The Temkin model explains this phenomenon better: the adsorption heat due to interactions with the adsorbate decreases linearly with the recovery rate during adsorption. The kinetic model of Elovich is applicable to this adsorption with $R^2 = 0.99$, the adsorption sites increase exponentially with the adsorption, which implies a multilayer adsorption. The pH variation showed that the adsorption increases with the increase of the pH and that the maximum adsorption is reached at pH = 12 which gave a yield of 96.19%. The adsorption phenomenon observed is endothermic and of a chemical nature. Unactivated corncobs are preferable to those activated thermally, the activation of which is also a source of environmental pollution.

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