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*Research Paper*

# ADSORPTION OF RHODAMINE B IN AQUEOUS SOLUTION BY ACTIVATED CARBON FROM THE SEED HUSKS OF *MORINGA OLEIFERA*

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This paper presents the results obtained from the use of activated carbon from the seed husks of *Moringaoleifera* for removal of two dyes namely Rhodamine B aqueous solution artificially contaminated. This study was undertaken to highlight certain parameters such as contact time, the adsorbent mass, pH, initial concentration of adsorbate and ionic strength. The test results show that satisfactory operating conditions are made at a time of balance equal to 40 minutes, a weight of 0.01 g adsorbate, a basic pH (9) and high initial concentrations. The adsorption isotherms are in agreement with the four models namely Langmuir, Freundlich, Temkin and DKR. But it is the Langmuir model that better describes the adsorption of our dye with a maximum adsorption capacity of 16.07 mg/g. Adsorption kinetics is slow, pseudo second order, with a value of adsorption constant $k_2$ equal to 0.423 g/min.g.

***Keywords:*** Adsorption, Charcoal, Shells *Moringa oleifera*, Rhodamine B

## INTRODUCTION

Pollution of the water environment of dyes can cause health risks to humans and their environment. The management of these involves the establishment of specific methods. Among them we can mention among others: chemical precipitation, electroplating, liquid - liquid extraction, coagulation-flocculation, reverse osmosis, electrodeposition, electrodialysis and adsorption (Slightly expensive, convenient and simple, one of the best methods for reducing pollutants at low concentrations) (Tchouchane *et al.,* 1991). Adsorption is a promising technique due to ease of use and low compared to other applications in the bleaching process cost, especially if the adsorbent is inexpensive and readily available. It is a method that this great advantage and good results in the retention of organic dyes (Juan *et al.,* 1997). Rhodamine B is a cationic dye of the xanthene family (Figure 1). It

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finds application in the textile, cosmetic, food (Abdella *et al.*) And tanneries. Rhodamine B is carcinogenic and can cause irritation, redness and pain of the eyes, lungs and skin (Nestmann *et al.,* 1979. Gupta, 2009). That's why its removal by adsorption on activated carbon has been considered in this work. In testing the efficacy of our activated carbon for retention Rhodamine B, various reaction parameters were considered (mass of the adsorbent, the pH, the initial content of adsorbate, and the model of sorption kinetics response best describes the process of sorption).

**Figure 1: Chemical Structure of Rhodamine B**
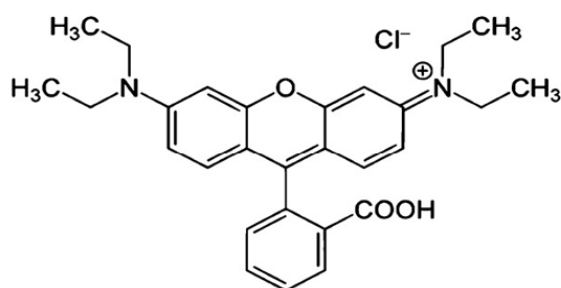


## MATERIALS AND METHODS

All solutions are prepared with distilled water. The Rhodamine B solution used in this work was prepared by dissolving 0.5 g of powder in Rhodamine 1000 mL of water for volume representing a final concentration of 500 ppm. And solutions girls for dilution. The pH adjustment is carried out of some solutions with solutions of NaOH and HCl. Coal obtained from the seed husks of *Moringaoleifera* is dried in an oven at 110°C for 24 h.

### Fabrication and Characterization of Activated Carbon

Activated carbon has been manufactured characterized in the laboratory of Physical and Theoretical Chemistry of Yaounde I. The characterization was made by bilait method of iodine calculation and Fourier transform IR.

The hulls of seeds of *Moringaoleifera* harvested dried and broken until the smaller particles to facilitate carbonization. These fragments are impregnated with phosphoric acid ($H_3PO_4$) to 10% with a ratio (r) equal to half.

$$r = \frac{m_{coque}}{m_{H_3PO_4}} = \frac{1}{2} \qquad ...(1)$$

After impregnation, these scraps are dried in an oven at a temperature of 110°C for 24 h this. Carbonization of our material is at 400°C for two (2) h with a heating rate of 10°C/min and the cooling is done gradually in a desiccator to room temperature. Once cooled, we wash with distilled water until a neutral pH and we again dry it in an oven at 110°C for 24 h. We then crushed in a mortar using a porcelain pestle both until a powder having a particle size less than 80 microns which constitute our powdered Activated Carbon (AC).

The iodine number and pH are determined in the order of: 497.439 mg/g and 6.68, respectively.

Interpretation of the IR spectrum (Figure 2) of the Fourier transformed a CA recorded shows a vibration band at 1713 cm$^{-1}$ corresponding to the stretching vibration of C = O bond of ketones. There is also a band at 1574 cm$^{-1}$ which indicates the presence of the C = C bond of the aromatic nuclei characteristic and the band at 1418 cm$^{-1}$ indicates the presence of the stretching vibration of CH bond shielded alkanes. The band at 1203 cm$^{-1}$ means the stretching vibration of C-O bond of the carboxylic acids. The signals at 889 and 909 cm$^{-1}$, respectively reflect vibration deformation and C = $CH_2$ and CH-plane deformation of alkenes.

**Figure 2: IR Spectrum of Activated Carbon**
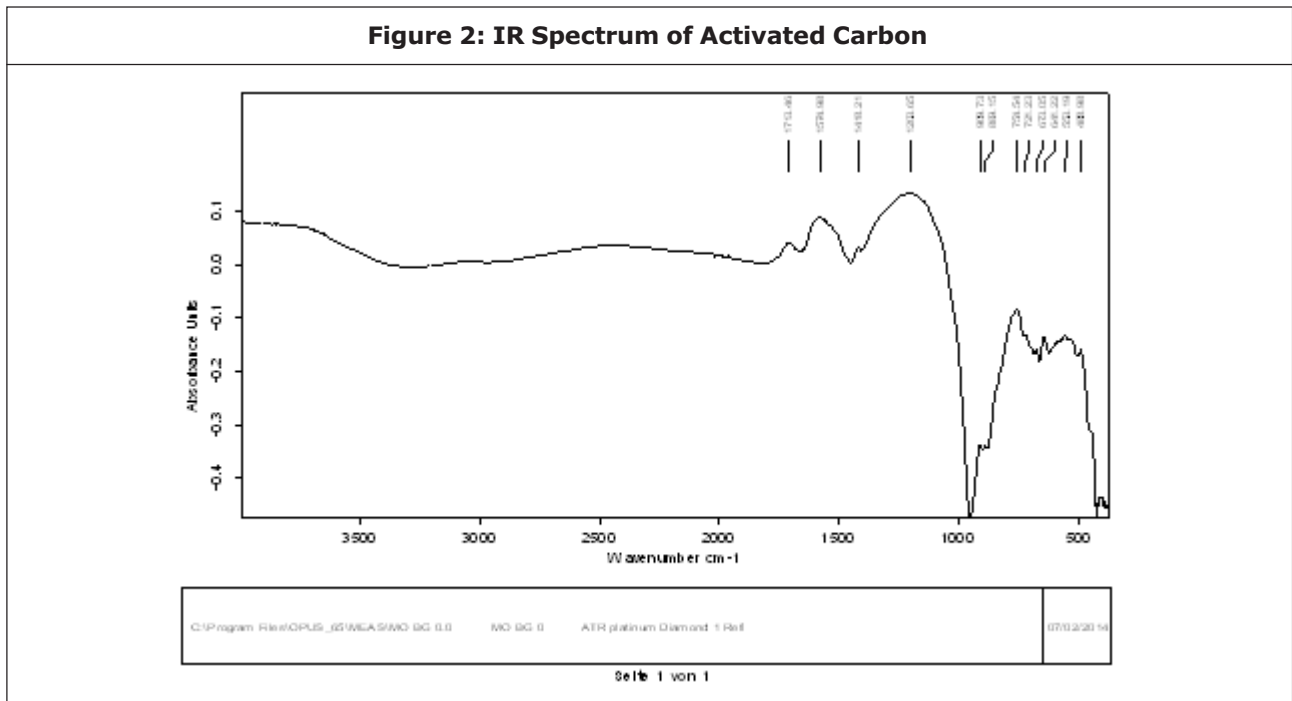


## Adsorption Tests

This part of our work the present study the influence of the operating parameters in the system (the mass of adsorbent in adsorbate concentration, pH) to yield the mono adsorption. For the measurement of the adsorption capacity, various masses of coal were mixed with 20 mL of a solution of Rhodamine B in a series of reactors and stirred for a set time using a magnetic stirrer over a bar magnet. The mixture after stirring was filtered and the filtrate determined by UV-visible spectroscopy has a wavelength λ equal to 555 nm obtained after a sweep. The adsorbed per unit mass of adsorbent (Qt) in the equilibrium amount of adsorption and the percentage (% R) are given by the following relationships:

$$Q_e = \frac{(C_O - C_e) \times V}{m} \qquad ...(2)$$

$$\% R = \frac{(C_o - C_e)}{C_o} \times 100 \qquad ...(3)$$

where

Qt: the amount adsorbed (mg/g);

Co: the initial concentration of the adsorbate (mg/L);

This means the concentration of the adsorbate at equilibrium (mg/L);

V: the value of the solution containing the adsorbate (mL);

m: the mass of adsorbent (g).

The values of various parameters varied during our trying vary as follows: the influence of the stirring time (0-60 min), the mass of activated carbon (0.01 to 0.1), pH (3-11) and the concentration of the Rhodamine B (0.2 - 9 ppm).

To investigate the adsorption power of our turnover, we applied the models Langmuir (4), Freundlich (5), Temkin (6) and Dubinin-Radushkevich-Kaganer (7).

$$\left.\begin{array}{l} \dfrac{C_e}{Q_e} = \dfrac{1}{Q_m K_L} + \dfrac{C_e}{Q_m} \\ ou \\ \dfrac{1}{Q_e} = \dfrac{1}{Q_m K_L C_e} + \dfrac{1}{Q_m} \end{array}\right\} \quad ...(4)$$

$$\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad ...(5)$$

$$Q_e = B\ln K_T + B\ln C_e \qquad ...(6)$$

$$\ln Q_e = \ln Q_{max} - \beta\varepsilon^2 \qquad ...(7)$$

where

Qe: Quantity equilibrium adsorbed (mg.g$^{-1}$);

Ce: concentration in the liquid phase at equilibrium (mg.L$^{-1}$);

Qm: Maximum quantity adsorbable (mg.g$^{-1}$);

$K_L$: Langmuir constant (L.mg$^{-1}$);

$K_f$ and n: Freundlich constants representing respectively the capacity and adsorption intensity.

B: is a constant related to the energy of adsorption (RT/bT);

bT: the adsorption potential is in J/mol;

Constant KT of the equilibrium binding (L/mg);

ε: potential Polanyi.

Finally, to examine the adsorption mechanism, the kinetic models of the pseudo first order, pseudo second order, Elovich and intra particle diffusion were used to test the dynamic experimental data.

$$\ln(Q_e - Q_t) = -K_1 t + \ln Q_e \qquad ...(8)$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} \qquad ...(9)$$

$$Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad ...(10)$$

$$\ln(P) = \ln K_{id} + a\ln t \qquad ...(11)$$
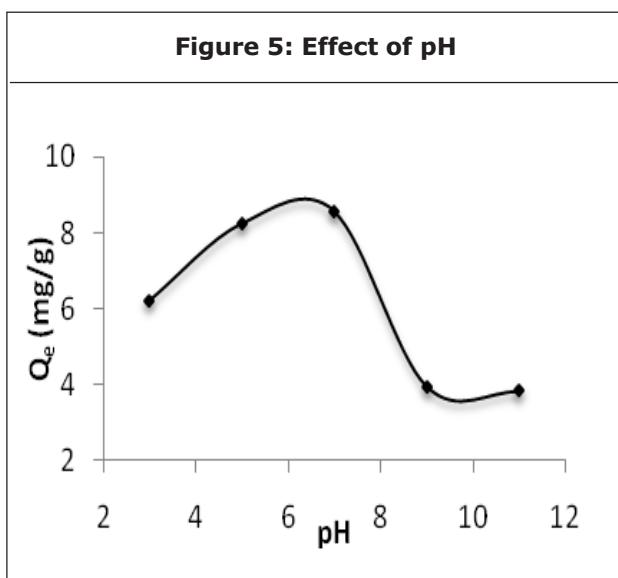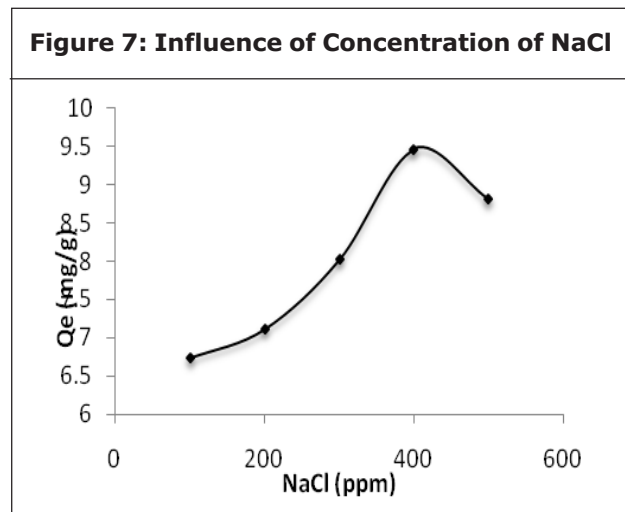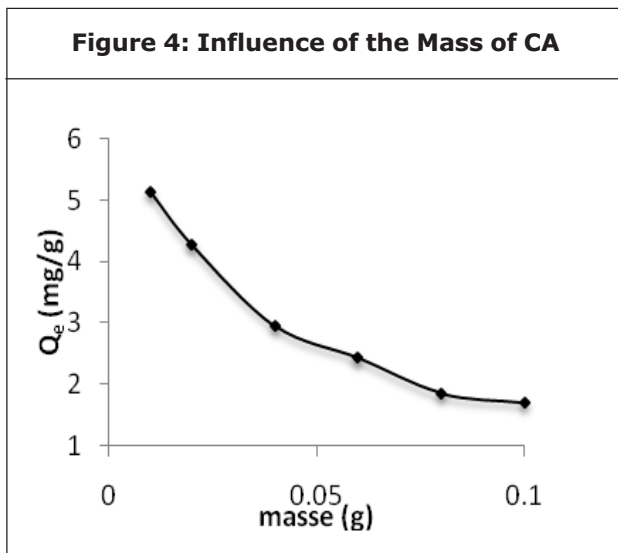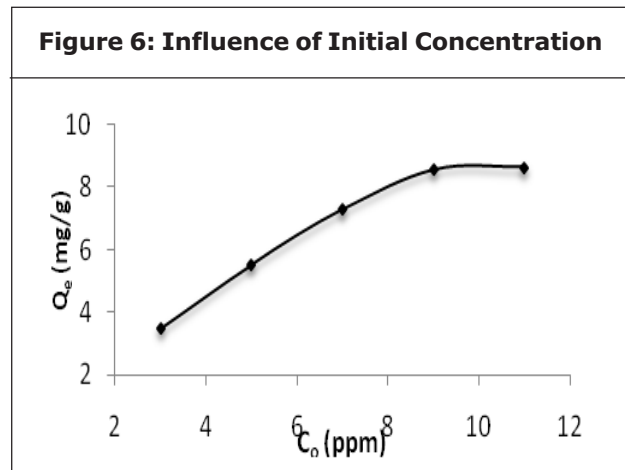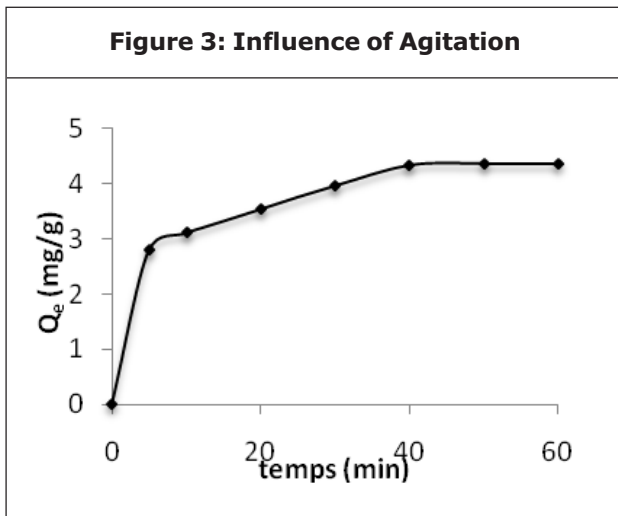
where

Qe: the amount adsorbed per unit weight of adsorbent at equilibrium (mg/g) species;

Qt: the amount adsorbed per unit mass of adsorbent at time t (mg/g) species;

$K_1$: rate constant pseudo-first-order min$^{-1}$;

$K_2$: the rate constant of second order adsorption mg.g$^{-1}$min$^{-1}$ processes nickname;

$\alpha$: is the initial rate of adsorption (mg/g min);

$\beta$: is a constant of desorption (g/mg);

P: is the retention rate;

$K_{id}$: is the rate constant of diffusion intra particulate, it may also be taken as the rate factor that is to say the percentage of adsorption per unit time;

a: is the gradient of the straight line, it depends on the adsorption mechanism.

## RESULTS AND DISCUSSION

### Influence of the Contact Time

Figure 3 shows that the amount adsorbed increases rapidly during the first minutes. This rapid growth is due to the availability of adsorption sites. The same trend is observed in the work of Sumanjit on the adsorption of rhodamine B (Sumanjit *et al.*, 2008). The amount adsorbed stabilizes from 40 min with a maximum amount adsorbed at equilibrium of 4.667 mg/ g. This stability reflects the establishment of equilibrium. This is due to the total occupation of adsorption sites initially available on the surface of our

**Figure 3: Influence of Agitation**



**Figure 4: Influence of the Mass of CA**



**Figure 5: Effect of pH**



**Figure 6: Influence of Initial Concentration**



**Figure 7: Influence of Concentration of NaCl**



turnover with rhodamine B. The same trend was obtained during the adsorption of Ni (II) smectite (Ketcha *et al.*, 2012) and during the adsorption of methyl orange by the CA (Karim *et al.*, 2012).

## Influence of the Weight of the Adsorbent

The number of slots and available ion exchange for adsorption depends on the amount of adsorbent in the adsorption process. It is apparent from this figure, for the other parameters constant the amount of Rh B adsorbed decreases with increasing mass of adsorbent. From 0.08 g of clay, the adsorbed amount of the dye is not moving. This behavior may be due to the number of adsorption sites, which decreases with the amount of adsorbent to the weight of 0.08

g at which the number of sites becomes stable (Gupta *et al.*, 2003. And Tsai *et al.*, 2007). This behavior can be explained by:

- As long as the amount of added adsorbent dye solution is low, the dye cations have easy access to adsorption sites. Uploading adsorbent increases the number of adsorption sites of the dye cations but more difficult to approach these sites because of congestion;

- A large amount of adsorbent creating agglomerations of particles, resulting in a reduction of the total surface area for adsorption, and therefore, a decrease in the amount adsorbed per unit mass of adsorbent.

## Effect of pH

From the Figure 5, we find that the amount adsorbed increases with the pH of the aqueous solution to the equilibrium pH is equal to 7 and decreases suddenly and tries to stabilize at around 10.

As the initial pH of the test solution is increased to 7, the number of adsorbent increases negatively charged molecules and promotes adsorption of the cation dye positively charged due to this electrostatic attraction. Thus a higher or lower pH is less adsorption. For this reason, pH 7, where the maximum observed adsorption, was chosen for the following experimental work.

The decrease of the quantity adsorbed increases as the pH that is to say greater than 7. This may be due to site occupancy by the anionic species that retard the ions approach to the surface of the adsorbent (Sankarl *et al.,* 2012).

The pigment removal kept constant from 10. The possible reason for this type of behavior is due to the fact that basic dyes are positively charged (Sumanjit *et al.*, 2008).

## Influence of the Initial Concentration

We are seeing an increase in the amount adsorbed when the initial concentrations ranging from 0.2 to 9 ppm. The adsorbed quantities ranging from 3.481 to 8.625 mg/g. The increase of the amount adsorbed with the initial dye concentration is explained by the fact that the initial concentration supplied significant forces to overcome any resistance of the mass transfer between-molecules of the aqueous solution and the surface of the AC. This increase of the amount adsorbed with the initial dye concentration is also due to the fact that increases the collision between the molecules and the dye adsorption sites (Uday *et al.*, 2006). Between 7 and 9 ppm the amount adsorbed varies very slightly and tends to stabilize due to this competition, which takes place between molecules of Rhodamine B and resulting in the total occupation or saturation CA sites available.

## Influence of Ionic Strength

The curves obtained in this study show that the addition of NaCl in one way or another during the adsorption of the two dyes. Initially the adsorbed amount of Rhodamine B in considerable increases with increasing the amount of NaCl added to 400 ppm and above this concentration is the reverse. It can be assumed that the thickness of the diffuse layer surrounding the activated carbon particles in an aqueous medium decreases as the ionic strength increases. Therefore, there is the approximation of the molecules activated carbon particles (Keren and O'Connor, 1982). Considering the results obtained, we can say that the addition of NaCl to 400 ppm decrease the solubility of Rhodamine B which subsequently promotes their increasing adsorption and beyond this concentration rather this addition increases the solubility which explains the decrease in the amount adsorbed.

## Study of the Adsorption Isotherm

The results obtained show that the isotherm is type I isotherm type I features a microporous adsorbent so the volume is particularly high. It is an isotherm that approximates the mathematical model of Langmuir. The values of all the constants and correlation coefficients $R^2$ Langmuir, Freundlich and Temkin DKR are summarized in Table 1 below.

The results obtained show that the Langmuir model best describes the adsorption of Rh B on the surface of CA because are close to unit.

Indeed, the Langmuir model indicates that we have a homogeneous distribution of the adsorption sites on the surface of our CA, more of the adsorption compound is our monolayer (Ferrandon *et al.*, 1995; Avom *et al.*, 2001). The essential feature of the Langmuir isotherm is the separation factor defined by Equation 12 (Hameed *et al.*, 2007). When it has a value between 0 and 1, the adsorption is favorable. This is the case because we rhodamine $R_L = 0.332$.

$$R_L = \frac{1}{1 + K_L \times C_O} \qquad ...(12)$$

The values of 1/n in the Freundlich model are both less than 1 This shows that the adsorption is carried out with great intensity characterized by a heterogeneity between the surface of the boards and our molecules dyes rolled identified a adsorption capacity of the AC high value of n for the two adsorbates is between 1 and 5 (Li *et al.*, 2010).

Temkin model which also has a good linear correlation coefficient shows us that our adsorption has a surface heterogeneity but also that the adsorption took place in multilayers.

The model DKR about shows him a good affinity with the process involved implying that we can have a homogeneous or heterogeneous distribution of adsorption sites and that there is no interaction between molecules adsorbate to the surface of the AC The values of the adsorption energy determined from the D-R-K model gives an indication of the type of adsorption. The adsorption energy value E is equal to 1000 kJ $mol^{-1}$. This experimental value is more than 80 kJ $mol^{-1}$, which implies that the adsorption of the dye on the CA is chemical type.

## Study of the Kinetics of Adsorption

Different linear correlation coefficients $R^2$ and constants derived speeds each kinetic model are reported in Table 2.

**Table 1: Correlation Coefficients and Constants of Langmuir, Freundlich, Temkin and K–D–R**

| Models | Langmuir | | | Freundlich | | | Temkin | | | D-K-R | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Paramètres | $K_L$ | $Q_m$ (mg/g) | $R^2$ | $K_f$ | n | $R^2$ | $K_T$ | B | $R^2$ | β | $Q_m$ (mg/g) | $R^2$ |
| Rh B | 0,224 | 16,07 | 0,987 | 3,327 | 1,764 | 0,934 | 2,421 | 3,306 | 0,961 | $5.10^{-7}$ | 2,194 | 0,976 |

**Table 2: Constant Speed and Correlation Coefficients of Kinetic Models**

| Models | Langmuir | | | Freundlich | | | | Temkin | | D-K-R | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Paramètres | $k_1$ (min$^{-1}$) | $Q_m$ (mg/g) | $R^2$ | $k_2$ (g/min.g) | Qe (mg/g) | $R^2$ | β | α | $R^2$ | a m².S$^{-1}$ | $K_{int}$ (mg.L.min$^{1/2}$) | $R^2$ |
| Rh B | 0,128 | 2,129 | 0,981 | 0,423 | 4,746 | 0,996 | 1,434 | 6,866 | 0,971 | 0,195 | 22,479 | 0,979 |

Given these results, we find that the elimination of Rh B by the AC is a good fit with the kinetic model of the pseudo second order which the correlation coefficient is about 0.996. This model reflects the existence of strong interactions between the surface of the CA and the adsorbate. We can thus say that we are in the presence of chemisorption (Idris *et al.*, 2012). It also has high values of correlation coefficients of other kinetic models (pseudo first order, Elovich and intra particle diffusion) that are above 0.9.

The kinetic model of the pseudo first order Elovich and show that the adsorption is multilayered, which corresponds to a chemisorption to form one or two layers ; translating a first adsorption layer, then the following layers for condensation ( Reddy *et al.,* 2010) .

Higher values of the correlation coefficients of the model show that particulate distribution within the adsorption process is diffusion controlled (within the pores of the CA). The low value of diffusion constant $K_{id}$ implies that the diffusion of Rh B (22.479 mg.L.min$^{1/2}$) is slow, which favors the formation of strong interactions between the Board and the adsorbate . But the value of the correlation coefficients of the model is smaller than those of the pseudo second order model, we can conclude that diffusion is not the limiting step in the adsorption mechanism. These results are in agreement with those of Belaid and Kacha on the kinetic and thermodynamic study of the adsorption of dyes (Belaid and Kacha, 2010 and Nadeen *et al.,* 2006).

## CONCLUSION

The objective of this study is to develop an agricultural residue. The seed husks of *Moringaoleifera* chosen in this study allowed after activation and carbonization at 400$^0$C for 2 h to obtain an activated carbon to iodine value equal to 497.439 and has a pH of 6, 68. The tests in batch mode allowed us to show that the adsorption of the mixture reaches equilibrium at 40 min with a retention percentage of 48.2% and is favored by concentrated solutions. The Langmuir isotherm best describes the adsorption processes involved and the kinetics of dye binding is best represented by the reaction model pseudo second.

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