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Research paper

Adsorption of Organic Dye Methylene Blue on Activated Carbon Prepared from Wood

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Abstract

Developing countries are the most exposed to pollution problems. To cope, they must develop integrated environmental management policies (water management, air treatment, treatment of industrial effluents, etc.). As a result, different treatment methods must be used to reduce these problems. This work aimed to evaluate the feasibility of fixing organic dye such as methylene blue using activated carbon (ACW) prepared from inexpensive precursor (sawdust) by chemical and thermal activation. The adsorption efficiency depends on several parameters such as the initial pH of the solution, the contact time and the mass of ACW. The adsorption isotherms were studied according to the Freundlich and Langmuir models, and the best was chosen on the basis of the comparison of their correlation coefficient results.

Keywords: *adsorption, activated carbon, methylene blue..*

1. Introduction

Methylene blue is the most common dye used in dyeing cotton, wood and silk. It can cause eye burns that cause permanent injury to humans and animals. Inhalation may cause breathing difficulties and ingestion through the mouth produces a burning sensation, nausea, vomiting, sweating and heavy cold sweats (Pro-Lab Diagnostics 2017).

The treatment of industrial waste containing this type of dye is of great interest.

A wide variety of physical, chemical and biological techniques have been developed and tested in the treatment of effluents filled with dyes. These processes include flocculation, precipitation, ion exchange, membrane filtration, irradiation and ozonation.

However, these processes are expensive and lead to the generation of large quantities of sludge (Robinson and all 2001).

Among the liquid discharge treatment processes, adsorption remains a relatively used and easy to implement technique. Activated carbon is the most widely used adsorbent because of its high adsorption capacity of organic materials (Baganea and all 2000)

From this perspective, the research then turned to treatment processes using less expensive natural materials. In this theme we will work on activated carbon made from red sawdust.

2. Materials and Methods

Methylene blue (BM). Methylene blue is a basic organic dye belonging to the family of thiazines. It is soluble in water and slightly in alcohol. It is used to study the performance of adsorbents in general and activated carbons in particular. The choice of this dye comes from the fact that it is organic in nature, cationic and of known average size (15A) (Madani M. 2014). The characteristics of the BM are summarized in Table 1.

The textile red. Textile red is an anionic dye (acid dyes), which makes it possible to dye certain fibers (polyamides for example) in an acid bath. It consists of chromophores, responsible for the coloring effect, and sulfonate or carboxylate groups that allow their solubilization in water. This class of dyes is important for the shades.

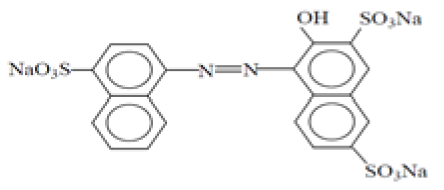
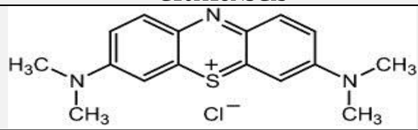


Figure 1: semi-developed formula of textile red (Roulia M. and al 2005).

Table 1: The different characteristics of BM dye (BENHAMED I. 2015)

Denomination	**Methyleneblue (BM)**
Chemical name	Chloride of 3,7-bis (dimethylamino) Phénaza-thionium
Gross formula	C16H18N3ClS
Semi-developed formula	
Molar mass	320g.mol^{-1}
Dimension (Diametre)	15A°
Area of the molecule	175A°^{2}
Lambda max	664nm

The adsorbent used. The adsorbent studied is an activated carbon prepared from red sawdust prepared in our laboratory (Tan I.A.W. 2007). Its physicochemical characteristics are presented in Table 2.

Table 2: The different characteristics of the activated carbon texture (Roulia M. and al 2005).

Porosity index (%)	Pore volume ($Cm^3.g^{-1}$)	Deviation ($Cm^3.g^{-1}$)	Actual density ($g.Cm^{-3}$)	Specific area ($m^2.g^{-1}$)
6.68	0.1367	0.0031	2.7811	703.37

2.1. Preparation of solutions

- Preparation of solutions of methylene blue and red

Stock solutions of (BM) at 2mg.L-1 and red at 60 mg.L-1 were prepared by respectively dissolving their salt in distilled water of volume 1L. The daughter solutions for the UV-Vis spectroscopic analysis tests were obtained by successive dilutions up to the desired concentrations. The pH of the solution is adjusted with a solution of hydrochloric acid HCl or sodium hydroxide while measuring these values using a pH meter.

- Preparation of nitric acid

We used a diluted $1mol.L^{-1}$ solution of nitric acid (HNO_3) prepared from 60% commercial HNO_3 solution and 1.38 density.

$$C=\frac{m}{M.V}=\frac{x.\varphi}{M}=\frac{x.d.1000}{M}$$

$$C=\frac{0,6*1,38*1000}{63}=13.14 mol.L-1$$

- Preparation of sodium sulphate Na2SO4

We prepared a solution of $0.1mol.L^{-1}$ sodium sulfate in a volume of 200mL.

$$C=\frac{n}{V}=\frac{m.}{M.V}$$

We know that:

- So the weighed mass is: m = C.V.M

Is : m = 0.1×200×10-3×142.04= 2.84g

Pollutant adsorption study on activated carbon. The adsorption tests were carried out at ambient temperature by placing in a beaker a fixed mass of 0.2 g of the active carbon and a volume of 50 ml of the solution containing the pollutant for an initial concentration and at a given pH. The whole is stirred with a magnetic stirrer for a period of 40 minutes to reach equilibrium. The mixture is then filtered and analyzed by UV spectrophotometry at the specific wavelength for each dye.

3. Results and Discussion

Preliminary study of red adsorption. Before we begin our study of the adsorption of methylene blue on activated carbon prepared from sawdust of red wood. A preliminary study was conducted to test the effectiveness of our activated carbon (ACW).

This study is carried out on the adsorption of methylene red and blue on three categories of substrates:

- Red sawdust in the rough

- Red sawdust activated with phosphoric acid (65%)

- Activated carbon made from red sawdust

The comparison of the results obtained on the three precursors is shown in Fig. 2.

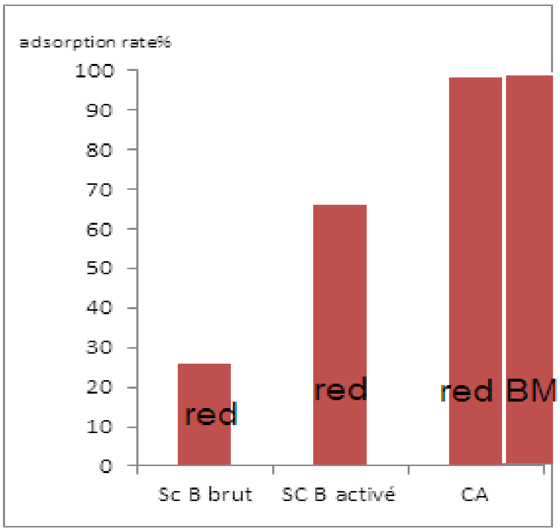


Figure 2: the adsorption rate of red and BM on different materials

From the figure above it is clear that the red sawdust in the raw state have a low adsorption rate of 25%. After chemical activation, this recovery rate is close to 65%. With activated carbon this rate is close to 100% and the same for BM is also close to 100%. It is therefore clear that in general chemical activation and more particularly chemical and thermal activation promotes and increases the adsorption capacity of the precursor.
In the following part we will study the adsorption of BM on activated carbon prepared from sawdust red wood, by studying the various parameters affecting the adsorption mechanism.

3.1. Methylene blue elimination study

This part of work aims to eliminate methylene blue by activated carbon prepared in our laboratory (Sakr F.and all. 2015). The experimental study focused on different parameters such as: adsorbent mass, pH and contact time.

3.1.1. Influence of contact time

The study of the adsorption of BM on activated carbon over time involves the determination of the time corresponding to the adsorption equilibrium or to a state of saturation of the support by the substrate.

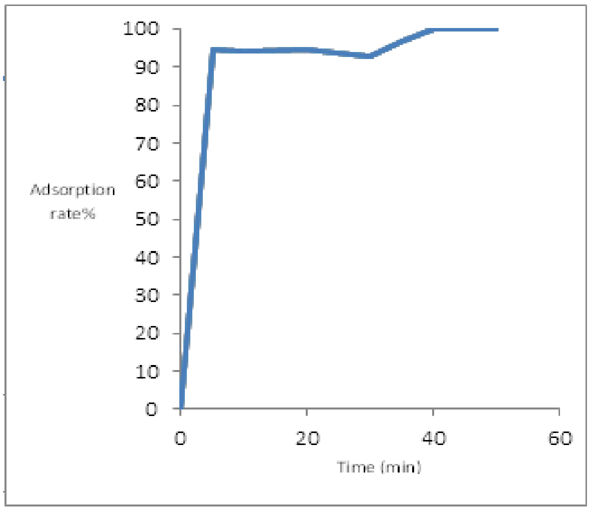


Figure 3: the adsorption rate of the BM on CA as a function of time, C0= 2mg.L-1; m = 0.01 g, pH = 4.17, V = 50 mL, T = 22 ° C.

The study of the influence of stirring time on the elimination of methylene blue (MB) (2 mg / L) over CA (0.2 g / L) was carried out for one hour of stirring. The results obtained (see Fig. 2) show that the removal efficiency of the BM increases with the stirring time and that a plateau corresponding to a maximum yield from 40 minutes appears. Indeed, the maximum elimination value of the BM corresponding to this time is 100%.

There are two stages during adsorption kinetics of BM on activated carbon powder. In the first step, a rapid increase, explained by rapid binding of BM molecules to the surface of the activated carbon powder, is the external mass transfer step. This transfer ensures the diffusion of the dye molecules on the surface of the ACW grains through a liquid film surrounding the adsorbent particles (El MERZOUKI K.. 2009 et Tan I.A.W. 2007).

- Study of isotherms of BM adsorption

The adsorption equilibrium data were adapted to the Langmuir and Freundlich isotherms at room temperature.

The Langmuir isotherm is based on the monolayer adsorption of chromium ions on the surface of activated carbon sites and is expressed in the following linear form (Elmerzouki K.and all. 2012):

$$\frac{1}{q_e} = \frac{1}{q_0\, b\, c_e} + \frac{1}{q_0} \qquad (1)$$

With: - Ce: equilibrium concentration (mg / L).

- qe: amount adsorbed at equilibrium (mg / g).

- q0: Langmuir constant represents the monolayer adsorption capacity (mg / g).

- b: empirical parameter related to the heat of adsorption (L / mg).

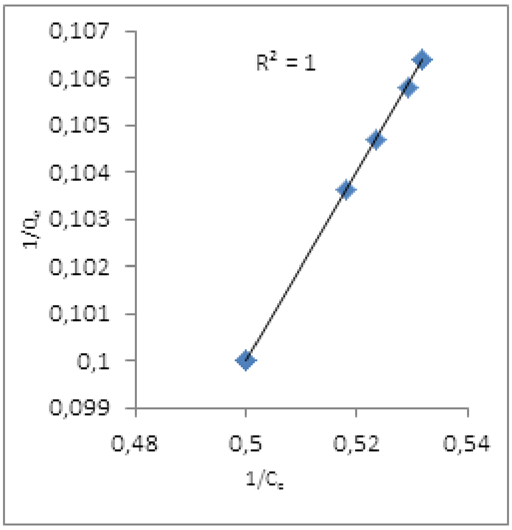


Figure 4: Langmuir isotherm of methylene blue on activated carbon

The Freundlich isotherm describes heterogeneous external energies by multilayer adsorption and is expressed in linear form (Mckay G..2003) with the following formula:

$$\ln q_e = \ln K_f + b_f \ln C_e \qquad (2)$$

With: - Kf: adsorption capacity (mg / g).

- bf: empirical parameter related to the intensity of the adsorption and which changes with the heterogeneity of the adsorbent.

For values in the range 0 <bf<1, adsorption is favorable (Mckay G.. 2003). The best results are obtained with bf close to 1.

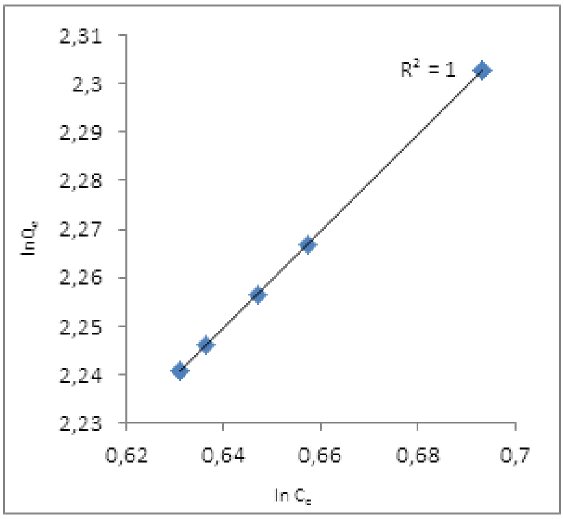


Figure 5: Freundlich isotherm of methylene blue on activated carbon

The results indicate that the BM adsorption phenomenon on ACW follows both Langmuir and Freundlich models since the calculated R^2 values are 1 in both cases.

pH effect.. The pH is an essential parameter to be taken into account in the dyes adsorption processes since it acts on the ionization state of the surface of the adsorbent.

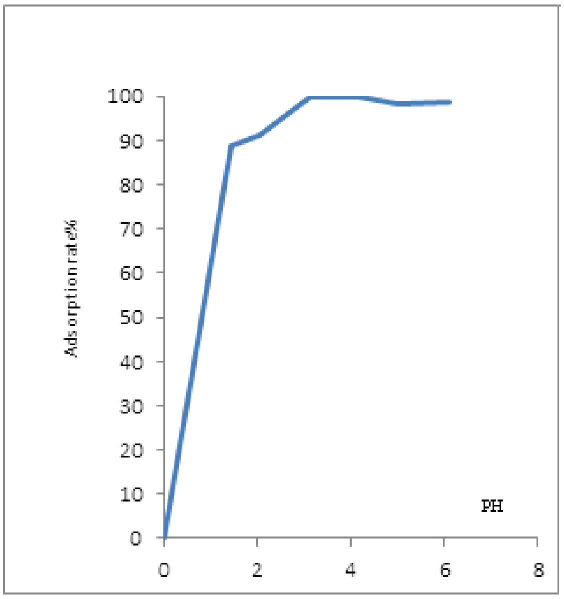


Figure 6: influence of pH on the adsorption of the dyes; C0 = 2mg.L-1; t = 40min; V = 50ml; m = 0.01g

For this study, samples of red dye solutions (2 mg / L) in contact with a mass of 0.2 g / L of ACW at different pH ranging from 0.5 to 6 were taken and stirred for one hour, then filtered and dosed. The results are presented below (see Fig. 6).

The curves show the variation of the adsorption capacity of the red adsorbed by the active carbons as a function of the pH. These results show that the acidic pH favors adsorption because its capacity is maximum of 100% at pH = 3. The similar behavior of adsorption with pH variation in solution has been reported in the literature (Boukraa A. and all. 2016).

The pH of the solution influences the surface of the adsorbent (Reffas A. 2010), as well as the degree of ionization of the pollutants. H_3O^+ hydronium ions and OH^- hydroxide ions are strongly adsorbed and influence the adsorption of other ions. The change in pH has a large effect on the adsorption process when binding the dye functional group to the active sites of the adsorbent surface. This, in turn, influences the kinetics of the reaction and the adsorption equilibrium characteristics.

In the aqueous solution, the dye studied is dissolved and converted into anionic ions. For acidic pH, the high adsorption rate is due to the large electrostatic attractions that exist between the positive charge on the surface of the adsorbent and the negative charge of the anionic dye (El MERZOUKI K.. 2009). For basic pH, there is competition between OH- anions and dyes for adsorption sites (Tan I.A.W And all. 2007).

3.1.2. Mass effect

It can be noted that good yields are obtained from a dose of activated charcoal powder of 0.1 mg / L. For a mass of 0.3 mg / L of activated carbon powder, the maximum elimination of BM reaches a value of 98.3%. For this part, the powder mass of activated carbon varies from 0 to 2 mg / L for an initial constant BM content (2 mg / L) and for 40 minutes of stirring. The results obtained show that the elimination of this dye increases with the introduced mass of activated carbon powder (see Figure 7). This is due to the increase in active adsorption sites attributed to the increase in adsorbent mass (Reffas A. 2010 et Madani M.. 2014).
Subsequently, it remains constant with increasing adsorbent mass.

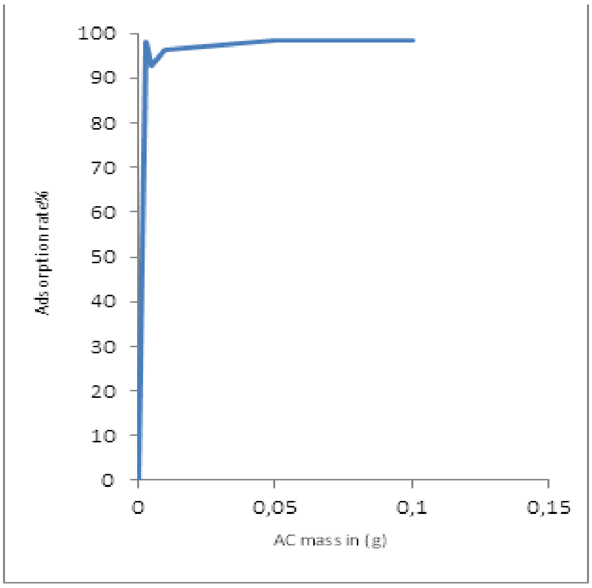


Figure 7: evolution of adsorption rate as a function of the mass of CA; C0 = 2mg.L-1; pH = 3; V = 50mL, T = 22 ° C; t = 40min.

4. Conclusion

In view of the results obtained during the adsorption of the dye (methylene blue) in synthetic solution on activated carbon, we can conclude that:

•The kinetics present globally two stages, the slowest appears only after about 5min. It corresponds to a diffusion mechanism in the porosity of activated carbon.

• Activated carbon gives better yields and reaches 100%.

This can be attributed to a large area, macroporosity and surface functions that retain the dye.

• The adsorption of the active carbon dye follows the laws of Freundlich and Langmuir with a maximum capacity of 10 mg / g.

• The optimum dose of adsorbent is a dose of 0.3 mg/L.

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