

Adsorption of Yellow Bemacid CM-3R Dye from Aqueous Solutions onto Raw and Sodium Bentonite

N. OUSLIMANI^{1,*}, F. ZIBOUCHE², A. IRATNI² and M.T. ABADLIA²

¹Laboratoire Des Traitements et Mises en Forme des Matériaux Fibreux. Faculté Des Science De L'ingénieur, Université M'hamed Bougara, Boumerdes, Algeria

²Unité de Recherche Matériaux Procédés et Environnement (UR-MPE), Faculté des Science de l'ingénieur, Université M'hamed Bougara, Boumerdes, Algeria

*Corresponding author: Fax: + 213 24 913866; Tel: +213 24 819424; E-mail: ouslimaniboumerdes@yahoo.fr

(Received: 16 February 2011;

Accepted: 14 October 2011)

AJC-10504

Discharges from the textile industries are heavily loaded with various dyes which requires their treatment. The most common method is to adsorb on solids high surface area, for example, clay material highly available and whose leaves are good natural adsorbents. In present study we used a local bentonite available in its natural form and sodium form for the adsorption of a dye CM-3R yellow bemacid provided by BEZEMA. The evaluation of the effect of various variables is driven by a series of experiments as the contact time, initial concentration of the dye, the initial pH. The different parameters show that the adsorption of the dye is favoured to 240 min, pH 2 and a temperature of 19 °C. The sodium bentonite yielded good performance results due to the improvement of its adsorption properties. The best correlation of experimental results are obtained with the Langmuir model for sodium bentonite ($R = 0.998$) and Freundlich for the raw bentonite (0997).

Key Words: Adsorption, Dye, Dye CM-3R yellow bemacid, Bentonite.

INTRODUCTION

Discharges from the textile industries are heavily loaded with dyes, which require their treatments. Even at low concentrations, they cause environmental problems¹. The methods most widely used to decolourize wastewater include physico-chemical methods, chemical and biological weapons, such as flocculation, coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques. However, wastewaters containing synthetic dyes are difficult to treat by conventional methods, since the dyes are generally stable under the effect of light and oxidants².

Adsorption is an effective process to remove dyes from textile waste. This process is cheap, simple, easy operation and insensitive to toxic substances². The most common method is adsorption on solids with high surface area, such as clays, available material and lower costs. Various studies on the use of adsorbents for cheap disposal of wastewater dyes were carried out on alumina, kaolinite³⁻⁵, montmorillonite⁶⁻¹⁰ and other materials¹¹⁻¹⁴.

Bentonite clays a cheap natural well known, available is considered an adsorbent because of its high adsorption capacity. Bentonite proved to be a promising material for removing

contaminants from wastewater. Bentonite is not only abundant, but it is really an effective and economical adsorbent for adsorption of pollutants, dyes. It belongs to the 2:1 clay family, which consists mainly of montmorillonite, the basic structural unit is composed of two layers of tetrahedral coordination of silicon ions surrounding an octahedral sheet sandwiched by aluminum ions.

Isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer results in a net negative surface charge on the clay. Compared to other types of clays, it has excellent adsorption properties and has adsorption sites available in the interlayer space and on the outer surface and edges¹⁵. Bentonite has a large area, provides an effective surface yellow. Previous studies have been conducted on the adsorption of cationic dyes as methylene blue^{1,5,9,10-13}, malachite green¹² maxilon yellow 4 GL^{3,8}, methyl violet³, GRL red maxilon⁸ for the removal of these dyes.

This study aims to evaluate the potentials of bentonite in removal of bemacid yellow dye CM-3R from aqueous solutions. The effects of contact time, initial concentration of dye, ionic strength, pH of solution, temperature and acid activation on the rate of adsorption of CM-3R bemacid bentonite were examined. The experimental data were analyzed.

EXPERIMENTAL

The bentonite used comes from the deposit Boughrara Hammam, (West Algeria). It is used in raw form and sodium form after being purified according to the protocol established by Naidja¹⁶. The X-ray spectrum (Fig. 1), shows that bentonite is a mixture of montmorillonite (JCPDS :00-003-0015), quartz (JCPDS : 01-085-0795), orthoclase (JCPDS : 00-008-0048), albite (JCPDS : 01-083-1613). The surface specific value is 55.186 m²/g at pH 9.48.

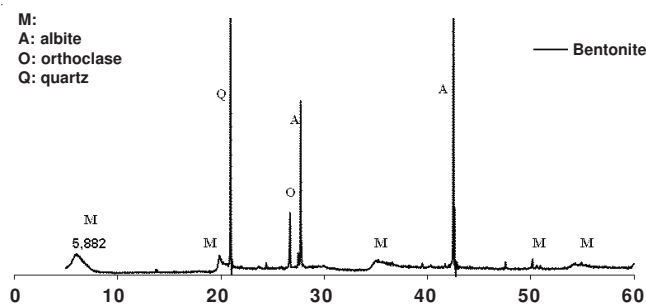


Fig. 1. XRD pattern of raw bentonite

The dye used is a yellow acid dye marketed under code yellow bemacid CM.3R provided by the Swiss company BEZEMA. It is used for dyeing wool and polyamide. It is a dye with high affinity Dyer.

Experimental methodology: A mass of 0.1 g of adsorbent (raw bentonite and sodium bentonite) is contacted in a series of vials with the dye solution at a concentration of 0.0264 mg / l in a volume of 20 mL at room temperature.

Analyses by UV/Visible allow to determine the residual concentrations of the dye by spectrophotometry and by using the calibration curve. The retention rate and the amount of dye adsorbed were determined from formulae (1) and (2).

$$TR \% = \frac{C_i - C_f}{C_f} \times 100 \quad (1)$$

$$Q = \frac{(C_i - C_f)}{m} \times V \quad (2)$$

where, TR is the dye retention rate in %; C_i is initial concentration of the dye mg /L; C_f is the equilibrium concentration mg /L; V is the solution volume in mL; Q is the quantity adsorbed mg/g.

A UV/Visible UNICA is used in the analysis to determine the residual concentrations of the dye by spectrophotometry and the calibration curve.

Effect of contact time: The determination of time for which the adsorption of dye onto the adsorbent is maximum was conducted between 30 and 300 min.

Effect of pH: The pH is an important variable because of its influence on the surface of bentonite. To assess the influence of this parameter on the adsorption of dye on the two types of bentonite, we conducted a series of tests carried out at pH values between 2 and 8.

Effect of temperature: The influence of the following temperatures: 19, 30 and 50 °C on the retention and adsorption of the dye by the two forms of bentonite was investigated.

RESULTS AND DISCUSSION

Influence of temperature and contact time: The results of retention rates and the amount of dye adsorbed are shown graphically in Figs. 2 and 3. These figures represent respectively the retention rate in % and the amount of dye adsorbed in mg/g. results show that: (i) whatever the form of bentonite, the elimination of the dye is not complete because the retention rates are 80.66 and 50.39 % respectively for sodium bentonite and bentonite gross (ii) The amount of dye adsorbed increases generally with time. However, saturation is reached at 4 h of treatment, whatever the form of bentonite. This adsorption of the dye is due to the crystallinity and swelling resulting from the presence of water molecules in the interlayer space of bentonite [2 and 9]. Sodium bentonite absorbs more dye and faster this is due to: (i) improving absorption properties of sodium bentonite, which contains all the same Na⁺ ions present on the surface of sheets⁹; (ii) the size of smaller particles resulting in a more developed surface area.

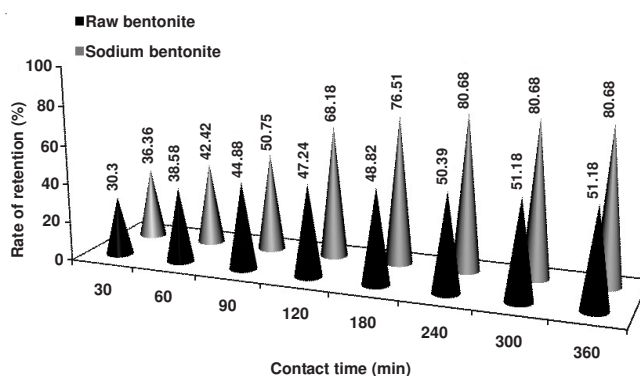


Fig. 2. Influence of contact time on the retention of the yellow dye Bemacid CM-3R by both raw and sodium bentonite

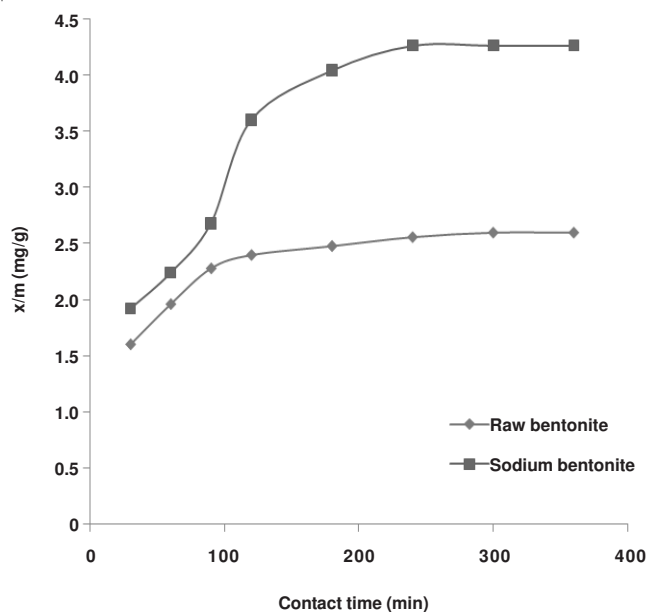


Fig. 3. Influence of contact time on the amount of yellow dye CM-3R Bemacid adsorbed by both raw and sodium bentonite

Furthermore, the acid treatment during purification has helped offset the negative charge of the sodium bentonite that

becomes positively charged which made easier the reaction with the dye anions for the acid attack and air links and frees space between the layers.

Effect of pH: The pH is an important variable because of its influence on the surface of bentonite. To assess the influence of this parameter on the adsorption of dye on the two types of bentonite, we conducted a series of tests carried out at values between 2 and 8. Retention rates and the amount of dye adsorbed is plotted on Figs. 4 and 5. The results obtained and the retention rate and the amount of dye adsorbed is influenced by pH. The best values are obtained at pH 2. Being an anionic dye and that initially the bentonite is negatively charged due to isomorphous substitutions, the results may be due to the dye affinity for metal ions such as Ca or Mg on the surface of the adsorbent¹⁷. According to coussement, the only possibility of anion exchange using bentonite would be replaced in the structure of the adsorbent OH ions by other anions¹⁸. Thus, in acid, some of the negative charge bentonite becomes positively charged so it's easy reaction with the anion of the dye and colours are present in neutral form, so this makes them less hydrophilic adsorption. Neutral molecules can even penetrate the lamellar space and move the water molecules between the layers aluminosilicate.

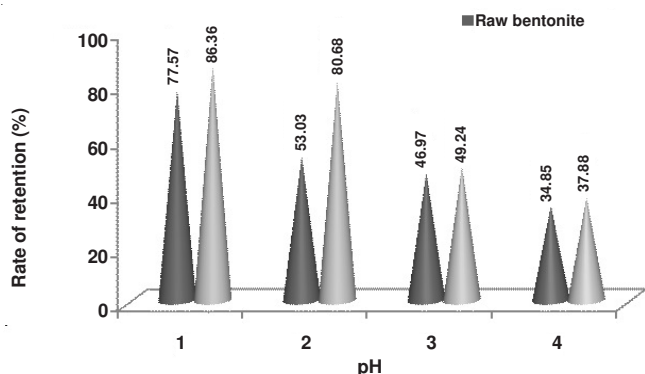


Fig. 4. Influence of pH on the retention of the yellow dye Bemacid CM-3R by both raw and sodium Bentonite

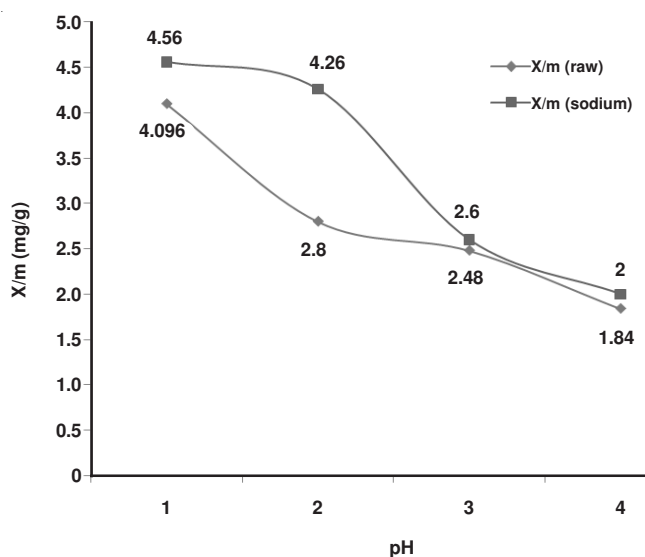


Fig. 5. Influence of pH on the amount of yellow dye CM-3R Bemacid adsorbed by both raw and sodium Bentonite

According to Wibulswars *et al.*¹⁹, low pH, the surface edges of the sheets bear a positive charge, this is due to the amphoteric sites that can be positively charged in acidic media and play a role because the edges are the AlOH groups and SiOH. These groups have an amphoteric behaviour in solution and may be potential binding sites. Sodium bentonite works best and this can be explained by its smaller size, hence a larger surface area.

Influence of temperature: The influence of the following temperatures: 19, 30 and 50 °C on the retention and adsorption of the dye by the two forms of bentonite was investigated. The experimental results are illustrated in Figs. 6 and 7.

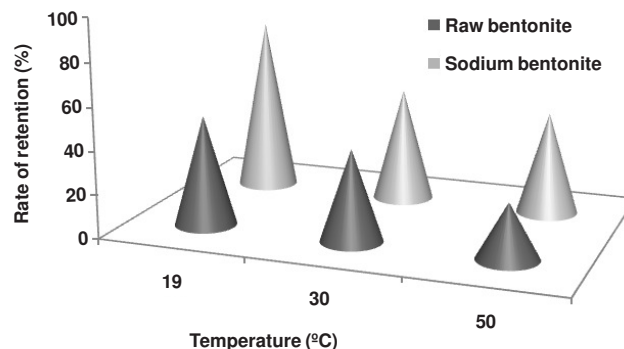


Fig. 6. Influence of temperature on the retention of the yellow dye bemacid CM-3R by both raw and sodium Bentonite

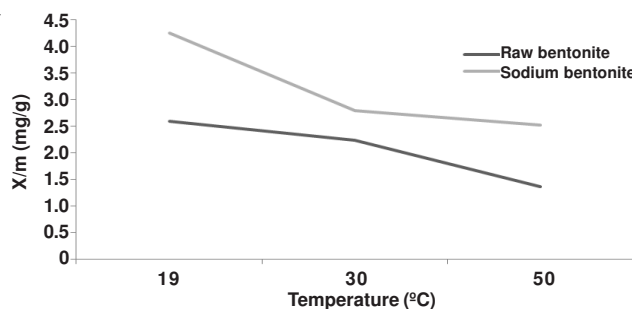


Fig. 7. Influence of temperature on the adsorption of the dye yellow Bemacid CM-3R by both raw and sodium Bentonite

Low temperatures seem to favour the adsorption of dye on the two forms of bentonite. In case of higher temperatures, we observe the decrease in the retention rate and the amount of dye adsorbed. This can be explained by desorption of the dye which implies exothermic phenomenon²⁰.

Influence of dye concentration: To study the adsorption isotherms of dye and sodium bentonite gross volume of 20 mL of concentration from 0.0132; 0.0264, 0.0528 to 0.1056 g/L are contacted with a mass of 0.1 g/L of adsorbent. The experimental conditions are: pH 2, temp., 19 °C and the time is 4 h.

Modeling of adsorption isotherms: The adsorption isotherms of dye on raw bentonite and sodium summers have studied the models of Langmuir²¹ and Freundlich²² whose formulae are presented below.

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$

$$Q_e = K_F C_e^{\frac{1}{n}}$$

where, Q_e : ultimate amount adsorbed in mg/g bentonite; K_L : Langmuir constant; K_F : Freundlich constant; C_e : dye concen-

tration at equilibrium; n: empirical constant related to adsorption intensity.

The operating results of each case *i.e.*, raw bentonite and sodium by Langmuir and Freundlich and the determination of ultimate capacity and adsorption coefficients K_L , K_F and n are present in Table-1.

TABLE-1
VALUES OF ADSORPTION PARAMETERS

Equation	Langmuir			Freundlich		
	q_m	K_L	R^2	K_F	n	R^2
Sodium bentonite	12.195	0.112	0.998	1.8407	0.467	0.945
Raw bentonite	4.629	0.156	0.882	0.6412	0.509	0.997

The resulting equation is a line of slope $1/q_m K_L$ and origin intercept $1/q_m$, two parameters for determining the equilibrium equation (2) *i.e.*, K_L and q_m . In the range of concentrations used, the adsorption isotherms are linear, with a correlation coefficient equal to 0.998 and the corresponding Langmuir adsorption model. Sodium bentonite retains more than the raw bentonite. The maximum adsorption capacity of sodium bentonite is 12,195 mg/g, while that of the raw bentonite is equal to 4.62 mg/g.

Conclusion

Raw bentonite and sodium bentonite used in this work are abundance and inexpensive in Algeria. The results obtained show that sodium bentonite should be retained as an adsorbent for the dye. It appear according to the results that the adsorption on both raw and sodium bentonite is favoured at pH 2, a temperature of 19 °C and a time of 4 h. The adsorption isotherms are linear, with a correlation coefficient equal to 0.998 and correspond to the Langmuir adsorption model. Sodium bentonite yielded good performance results due to

the improvement of its adsorption properties. The best correlation of experimental results are obtained with the Langmuir model for sodium bentonite ($R\% = 0.998$) and Freundlich for the raw bentonite (0.997).

REFERENCES

1. B.H. Hameed and A.A. Ahmad, *J. Hazard. Mater.*, **164**, 870 (2009).
2. A. Gücek, S. Sener, S. Bilgen and M.A. Mazmanci, *J. Colloid. Interface Sci.* **286**, 53 (2005).
3. M. Dogan, M.H. Karaoglu and M. Alkan, *J. Hazard. Mater.*, **165**, 1142 (2009).
4. M.H. Karaoglu, M. Dogan and M. Alkan, *Micropor. Mesopor. Mater.*, **122**, 20 (2009).
5. M.H. Karaoglu, M. Dogan and M. Alkan, *Desalination*, **256**, 154 (2010).
6. A.H. Gemeay, A.S. El-Sherbiny and A.B. Zaki, *J. Colloid. Interface Sci.*, **245**, 116 (2002).
7. Erdal Eren, *J. Hazard. Mater.*, **162**, 1355 (2009).
8. Meral Turabik, *J. Hazard. Mater.*, **158**, 52 (2008).
9. A. Özcan, Ç. Ömeroglu, Y. Erdogan and A. S. Özcan, *J. Hazard. Mater.*, **140**, 173 (2007).
10. A.S. Özcan, B. Erdem and A. Özcan, *J. Colloid. Interface Sci.*, **280**, 44 (2004).
11. A. Özcan, E.M. Öncü and A.S. Özcan, *J. Hazard. Mater.*, **129**, 244 (2006).
12. I. Chaari, M. Feki, M. Medhioub, J. Bouzid, E. Fakhfakh and F. Jamoussi, *J. Hazard. Mater.*, **172**, 1623 (2009).
13. J.W. Sheng, Y.N. Xie and Y. Zhou, *Appl. Clay Sci.*, **46**, 422 (2009).
14. R.C. Liu, B. Zhang, D. Meia, H.Q. Zhang and J.D. Liu, *Desalination*, **268**, 111 (2011).
15. F. Luckham and S. Rossi, *Adv. Colloid. Interf. Sci.*, **82**, 43 (1999).
16. A. Nadja, Université de Haute-Alsace (1988).
17. S. Coussi. Ph.D. Thesis, The University of Paris V, France (1980).
18. C. Wonwook and Y.C. Kenneth, *J. AWWA*, **10**, 562 (1976).
19. R. Wibulswas, D.A. White and R. Rautiu, *Environ. Technol.*, **19**, 627 (1998).
20. C.E. Chitour, Physico chimie des surfaces. L'adsorption gaz-solide et liquide-solide Tome II (2004).
21. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
22. H. Freundlich, *Z. Phys. Chem.*, **57**, 385 (1906).