Removal of Anionic Dye by Natural Algerian Montmorillonite

Djelloul Bendaho*, Tabet Ainad D and Djillali B

Laboratory of Organic Chemical-physical and Macromolecular Faculty of Exact Sciences, University Djilali Liabès, Faubourg Larbi Ben m'hjdi P.O.Box. 89, Sidi Bel-Abbès 22000, Algeria

Abstract

Adsorption of methyl orange (MO) using an Algerian montmorillonite has been investigated. Which was used for the first time like an adsorbent for removing anionic dye from aqueous solution, the influences of several parameters such as contact time, adsorbent dose, pH and temperature on the adsorption of methyl orange have been tested. The results showed that nearly 40 min of contact time are found to be sufficient for the adsorption to reach equilibrium. The residual concentration of the dye is determined using UV/Vis Spectrophotometer at wavelength 464 nm. Langmuir and Freundlich isotherm models were used to describe adsorption data. Adsorption kinetics was best described by the pseudo-second order model.

Keywords: Dye; Adsorption; Clay; Adsorption kinetics; Adsorption isotherms

Introduction

The use of synthetic chemical dyes in various industrial processes, such as food, paper, plastic, textile, etc. are one of the most problematic water pollution causes [1]. Discharge of wastewater into natural streams and rivers from the industries using dyes poses severe environmental problems because they are usually very recalcitrant to microbial degradation. Dyes in surface waters are of barrier effect on the sun light penetration and aeration of water body, and thus reduce photosynthetic activity [2]. For these reasons, several methods are used for eliminating the excess of colored organic pollutants from process or wastes effluents including biological treatments, however, unsatisfactory results were achieved by these techniques, such as coagulation-flocculation based on the addition of coagulant and flocculants (aluminium salts and polymers) [3], but coagulation generates chemical sludge and doesn't remove acid and reactive dyes of low molecular weight. Biological treatment may involve aerobic and anaerobic degradation by microorganisms [4]. Adsorption using activated carbon or ion exchange resins is the most popular technique for dyes removal due to its efficiency but the activated carbon cannot adsorb dispersed and pigmented, dyes nevertheless these methods are not satisfying because of the weak colorant biodegradability [5,6]. Other new processes electro coagulation, advanced oxidation processes, and adsorption were elaborated to meet the required standards. Among these techniques, adsorption is considered as the most efficient technology for the removal of dyes using local materials.

In this way the majority of the processes are very selective according to the colorant categories to treat and some just move the pollution instead of removing it. It is necessary for the process to mineralize the colorant. Recent investigations by several researchers proved onto use of low-cost, reusable, locally available, biodegradable adsorbent made from natural sources like waste orange peel, banana with cotton waste, rice husk, agriculture waste residues and bentonites clay [7]. The different applications of the clay depend on their specific adsorption properties, the ion exchange and the surface nature [8]. Due to these qualities, clay is used in different field, like in medical and pharmaceutical industries, organic molecule polymerization [9,10], and pollutant retention such as pesticides, organic, inorganic compounds, heavy metals [11].

The originality of this present work is to compare the performance and capacity of adsorption of methyl orange from different clays. Indeed, we propose to evaluate the removal efficiency of methyl orange in aqueous solution by adsorption using raw Algerian MMT clay. The essential parameters of the adsorption process, mainly contact time,

mass of clay, temperature, initial concentration of dye, and pH of the aqueous solution were determined and optimized. The equilibrium of adsorption was modelled by using the Langmuir and Freundlich isotherm models, the kinetic parameters and intra-particle diffusion were also then determined for the methyl orange – Algerian MMT-system.

Materials

Preparation of MMT clay

The clay used in this work is montmorillonite (MMT) type from Tiout region, this last was suspended in distilled water and maintained under constant stirring for 2 hours to release impurities. The suspension was then filtered and dried at 105°C to constant dry weight, then stored in a securely closed flask against the moisture.

Dyes

In order to show the Algerian MMT clay capacity of decoloration, we chose an organic colorant that it has methyl orange is an intensely colored compound used in dyeing and printing textiles. It is also known as C.I. Acid Orange, dye was purchased from Sigma Aldrich, heterocyclic aromatic chemical compound, having the chemical formula $C_{14}H_{14}N_3NaO_3S$ and molecular weight of 327.33 g/mol. The structure of direct dye was given in Figure 1.

Figure 1: Chemical structure of methyl orange dye.

***Corresponding author:** Djelloul Bendaho, Laboratory of organic chemical-physical and macromolecular Faculty of exact sciences, University Djilali Liabès, Faubourg Larbi Ben m'hjdi P.O.Box. 89, Sidi Bel-Abbès 22000, Algeria, Tel: 213-077-174-9785; E-mail: bendaho_djelloul@yahoo.fr

Received December 16, 2014; **Accepted** February 12, 2015; **Published** February 25, 2015

Citation: Bendaho D, Tabet Ainad D, Djillali B (2015) Removal of Anionic Dye by Natural Algerian Montmorillonite. J Environ Anal Chem 2: 130. doi:10.4172/2380-2391.1000130

Copyright: © 2015 Bendaho D, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Characterization of MMT clay

Chemical analysis showed the clay used is composed essentially of silica and alumina approximately 71.5% and of iron oxide 7.30% , Chemical compositions in mass % of raw clay obtained are listed in Table 1, the presence of ions Na^+ , Ca^+ and K^+ in the clay gives it a swelling type. The ratio $\text{SiO}_2/\text{Al}_2\text{O}_3=3.51$ reveals its montmorillonite characteristics it have both Bronsted and Lewis acid sites and when exchanged with cations having a high charge density, in the other hand (Table 1) samaruzed difference between Algerian MMT and other MMT such as American and French. Raw clay from Algerian has 5.68% more SiO_2 than (Vienne, France) and 1.68% less SiO_2 than (Wyoming, USA), in the other hand the Algerian MMT contains 5.42% and 5.32% less Al_2O_3 than the Wyoming and Vienne bentonites, respectively.

Qualitative analysis of Algerian MMT is performed by FTIR transmission spectra using KBr technique. The analysis was carried out

Elements	Wyoming USA	Vienne French	Tiout Algeria
SiO_2	57.40	50.04	55.72
Al_2O_3	20.27	20.17	15.85
Fe_2O_3	2.92	0.68	7.30
FeO	0.19	9	-
CaO	0.23	1.46	4.11
MgO	3.13	0.23	2.26
K_2O	0.28	1.27	4.08
Na_2O	1.32	traces	1.30
TiO_2	0.12	0.16	-
SO_3	-	-	0.43
$\text{SO}_{3\text{yp}}$	-	-	1.11
H_2O	6.85	26	-
Cl ⁻	-	-	0.01
PF	-	-	7.66

Table 1: Comparison of the Composition (in %) of American, French, and Algerian MMT.

Assignment	Raw TN clay cm^{-1}
Al-OH	3620
H-OH stretching (for H_2O)	3435
Si-O-Si stretching	1031
H-OH bending	1638
Si-O stretching (for silice)	797
Si-O-Al	531
Si-O-Mg	467
Fe_2O_3	2071

Table 2: FTIR spectra data of raw Algerian clay.

on Perkin Elmer precisely Spectrum One FT-IR Spectrometer in the wave number range of $400\text{--}4000\text{ cm}^{-1}$. The FTIR spectrum of TN clay was showed in Figure 2 and the FT-IR results are represented in Table 2.

The mineralogical composition of the montmorillonite was performed on by X-ray diffraction (XRD) using DRX.D8 ADVANCE (BRUKER) X-Ray powder diffractometer operanting with $\text{K}\alpha$ radiation of Cu ($\lambda = 1,5406\text{ \AA}$), and 2θ ranging from 2° to 80° . The Xray spectrum shows that the Algerian raw clay is a mixture of monmorillonite and impuretes of calcite and quartz (Figure 3).

Adsorption experiments

Adsorption experiments were carried out at room temperature ($22 \pm 2^\circ\text{C}$). Approximately 80 mg of Algerian montmorillonite (MMT) was weighted into 100 ml glass containers and brought into contact with 50 ml of dye solution with predetermined initial dye concentrations C_0 . The obtained suspensions were maintained under constant magnetic stirring during the necessary time to reach adsorption equilibrium. The adsorption tests are perfumed at natural pH, room temperature and stirring at different time intervals. After equilibrium, the aqueous phase was separated by centrifugation. The concentration of the residual dye was determined using a UV-Vis spectrophotometer (SHIMADZU 1240) at 664 nm. The adsorption equilibrium capacity (q_e) (mg/g) was calculated from the following equation:

Figure 2: FTIR spectra of raw Algerian clay.

Figure 3: XDR result for raw Algerian clay.

$$q_e = (c_0 - c_e) \cdot v/m \quad (1)$$

q_e : is the amount of dye adsorbed at equilibrium (mg/g).

C_0 and C_e are the initial and equilibrium concentrations of the dye, respectively (mg/l).

V : is the volume of the solution (l).

m : is the mass of the adsorbent (g).

Results and Discussion

Effect of contact time

The influence of time is achieved at natural pH of the solution for an initial dye concentration 26.186 mg/l, with 80 mg/l of raw clay and room temperature. The amount of colorant adsorbed q_t at time t was determined by the following expression:

$$q_t = (c_0 - c_t) \cdot v/m \quad (2)$$

Where;

q_t is the amount of dye adsorbed at time t (mg/l)

C_0 and C_t are the concentrations of the dye at initial ($t=0$) and at time t , respectively.

Figure 4 shows the time course of adsorption equilibrium of methyl orange onto raw clay. The amount of dye adsorbed by adsorption on raw clay was found to be rapid at the initial period between (0-40 min) of contact time and then become slow and stagnant with increase in contact time (40-180 min). This was due to the fact that, at the initial stage the number of free adsorption sites was higher, and the slow adsorption rate in the later stage was due to slower diffusion of solute into the interior of the adsorbent [12,13]. The maximum adsorption occurred after 60 min and there was almost no adsorption beyond this time.

Kinetics order

The kinetic studies describe the rate of adsorption and this rate controls the equilibrium time. These kinetic models are useful for the design and optimization of effluent treatment models. Pseudo first order, pseudo second order,

The second order kinetic model has the following formula.

$$\frac{dq}{dt} = k \cdot (q_e - q_t)^2 \quad (3)$$

Where k is the rate constant of second-order adsorption has the following formula.

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k \cdot t \quad (4)$$

For the pseudo-second-order model is given by the following equation.

$$\frac{dq_t}{dq_e} = k' \cdot (q_e - q_t)^2 \quad (5)$$

Where k' is the rate constant of pseudo-second-order adsorption has the following formula.

$$\frac{t}{q_t} = \frac{1}{(k' \cdot q_e^2)} + \frac{t}{q_e} \quad (6)$$

The kinetic data obtained using the second order and pseudo-second order is depicted in Figures 5 and 6. The q_e value calculated from the pseudo-second-order model is in accordance with the experimental

Figure 4: The effect of contact time on the adsorption of MO on Algerian MMT.

Figure 5: Plot of t/q_e versus t from the pseudo-second-order model.

Figure 6: Plot $1/q_e - q_t$ versus t from the second-order model.

q_e value. The correlation coefficient R^2 of the linear plot is very high. The result is shown in Table 3. The value of kinetic constant and q_e indicates that the adsorption follow the pseudo-second order model. Several studies found that the kinetics of adsorption of dyes on clay supports obey to the pseudo-second-order [14-17].

Effect of adsorbent mass

The effect of adsorbent dosage on the adsorption process can be carried out by preparing adsorbent-adsorbate solution with different amount of adsorbents (1-4 g/l) added to fix initial dye concentration (26.186 mg/l), room temperature, pH natural and shaken together until equilibrium time. The effect of sorbent quantity on dye removal is illustrated in Figure 7. From the figure it can be seen that an increase mass of crude clay 1g /l down to a value of 4 g / l causes a decreases in residual dye concentration. The increase in methyl orange adsorption with the increase in adsorbent mass is attributed to increase in surface area of micro pores and the increase in availability of vacant adsorption sites. Similar results have been reported for the adsorption of methyl orange on Algerian MMT [18-20].

Effect of pH

The pH is one of the most important factors controlling the adsorption of dye onto adsorbent. The influence of pH on dye removal was determined by performing the adsorption experiments at different initial pH of the solution (2-11) at room temperature. The pH had been adjusted to the desired value with HCl (0.1 N) and NaOH (0.1 N) solutions by using a HANNA 210 pH-meter equipped with a combined pH electrode. The adsorption of methyl orange onto clay is highly dependent on pH of the solution.

Figures 8 and 9 shows the influence of the pH of the initial dye solution on the adsorption capacity of MO on Algerian MMT. As the pH value increased from 2.0 to 6.0, the adsorption capacity of dye onto Algerian MMT rapidly decreased. The removal dye is higher in the acid pH region because the MO acid dye give negatively charged ions when dissolved in water, the adsorption of MO dye is facilitated on positively charged surface of sorbent at $pH < pH_{pzc}$.

Parameters	Pseudo-second-order
K' (g/mg min)	5.218
$q_{e,cal}$ (mg/g)	9.107
$q_{e,exp}$ (mg/g)	9.141
R^2	0,99

Table 3: The pseudo- second -order parameters of MO adsorption into Algerian MMT.

Figure 7: The effect of adsorbent mass on the adsorption of MO on Algerian MMT.

Figure 8: The effect of pH of the solution on the adsorption of MO on Algerian clay.

Figure 9: The effect of the temperature on the adsorption of MO on Algerian MMT.

In contrast, at a high pH solution the capacity of dye removal will decrease for anionic dye adsorption [21]. Because when the pH of dye solution is increased the surface tends to acquire negative charge, thereby resulting in a decreased adsorption of dyes due to decreasing electrostatic force existing between the negatively charged sorbate and positively charged sorbent.

Effect of temperature

The amount of dye adsorbed on Algerian MMT was determined at 20, 30, 40 and 60°C to investigate the effect of temperature. 80 mg of adsorbent was added to 50 ml dye solution with initial concentration of 26.186 mg/l. The contents in the flasks were agitated for 40 min.

The decrease in the adsorption capacity of methyl orange with increasing temperature results from the weakening of adsorptive forces between the active sites on the molecule and the Al-Si-Mg anion of the dye, but also between the molecules dye and the adsorbed phase [22].

Thermodynamic parameters

The Gibbs energy ΔG is calculated from the given equation:

$$\Delta G = -RTL \ln K_c \quad (7)$$

K_c represented the ability of the retain of the adsorbate and extent of movement of it within the solution. The value of K_c can be deduced from the following formula:

$$K_c = \frac{q_e}{c_e} \quad (8)$$

Where:

q_e : is the amount of dye adsorbed at equilibrium (mg/g)

C_e : is the equilibrium concentration of the dye in the solution.

The thermodynamic equation:

$$\Delta G = -RTL \ln K_c \quad (9)$$

And the Vant'Hoff formula:

$$\Delta G = -RTL \ln K_c \quad (10)$$

Can be deduced the following formula:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{R} \cdot \frac{1}{T} \quad (11)$$

The values ΔS and $\ln K_c$ can be obtained by plotting the $\ln K_c$ versus $1/T$ (Figure 10).

According to the thermodynamic parameters represented in Table 4 we realized that the ΔH enthalpy of the system is negative so the adsorption process on Algerian MMT is exothermic, the low value of the enthalpy ΔH energy (<20 KJ/mole) shows that it is a physical adsorption, the physisorption is generally considered to be an effective method for quickly lowering the concentration of dissolved dyes in an effluent, Adsorption takes place in multilayer, The negative values of

Adsorbent	Colorant	T(K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol .K)	R^2
Algerian MMT	MO	293	-4.251	-2.241	6.862	0.96
		303	-4.320	-	-	
		313	-4.388	-	-	
		323	-4.457	-	-	
		333	-4.526	-	-	

Table 4: Thermodynamic parameters of MO adsorption into Algerian clay.

Figure 10: plot of $\ln K_d$ versus $1/T$ for the estimation of thermodynamic parameters.

Langmuir	$Q_{max} = 27.824$	$b = 1.2397$	$R^2 = 0.99$
Freundlich	$\log K_F = 0.208$	$1/n = 0.64$	$R^2 = 0.96$

Table 5: Isotherm constants for adsorption of methyl orange into Algerian MMT.

Adsorbent	adsorbate	Adsorption capacity (mg/g)	Reference
Bentonite	Malachite Green	7.716	Tahir and Rauf [17]
Bentonite algeria	Rouge bezanyl	39.11	Benguella and Yacouta-Nour [18]
Na-Bentonite And Ca-Bentonite	Basic Violet 14	147.9 and 100	Jiang et al.
Crude And Purified Clay	Methylene Blue	50 and 68.5	Karim et al.
chitosan intercalated montmorillonite	Methyl orange	70.42	Chakkrit Umpuch and
Natural ClayCu(II)-Loaded MMT	Crystal Violet	25 and 42	Songsak Sakaew In this study
Algerian clay MMT	Metlyl orange	27.86	

Table 6: Comparison of the adsorption capacity of dyes onto adsorbents such as clay.

ΔG° for Algerian MMT adsorbent at various temperatures indicate the process to be feasible and spontaneous. Actually that the values of the ΔG° decrease with increasing temperature shows the increase of spontaneous influence [23].

Adsorption isotherms and models

An adsorption isotherm is the presentation of the amount of solute adsorbed per unit weight of adsorbent as a function of the equilibrium concentration in the bulk solution at constant temperature. Langmuir and Freundlich adsorption isotherms are commonly used for the description of adsorption data.

The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. The homogeneous Langmuir adsorption isotherm is represented by the following equation.

$$q_e = q_{max} \cdot bC_e / (1 + bC_e) \quad (12)$$

Where q_e is the amount adsorbed at equilibrium (mg/g), C_e the equilibrium concentration (mg/l), b a constant related to the adsorption energy (l/mg), and q_{max} the maximum adsorption capacity (mg/g).

The linear form of Langmuir equation may be written as.

$$q_e = C_e^{1/n} \cdot K_F \quad (13)$$

By plotting $(1/q_e)$ versus C_e , q_{max} and b can be determined if a straight line is obtained.

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces, and adsorption capacity is related to the concentration of colorant at equilibrium. The heterogeneous Freundlich adsorption isotherm is represented by the following equation:

$$q_e = C_e^{1/n} \cdot K_F \quad (14)$$

Where the K_F is Freundlich constant related to the adsorption capacity (mg/g) and $1/n$ is indicative of the energy or intensity of the reaction and suggests the favourability and capacity of the adsorbent/adsorbate systems (l/mg).

The linear form of Freundlich equation may be written as

$$\log q_e = \frac{1}{n} \cdot \log C_e + \log K_F \quad (15)$$

The values of K_F and $\frac{1}{n}$ can be determined by plotting the $\log q_e$ versus $\log C_e$, if a straight line is obtained.

The isotherm parameters for the adsorption of MO onto Algerian MMT are summarised in Table 5. It can be seen, the result revealed that the adsorption of methyl orange dye onto Algerian MMT was the best-fit both Langmuir and Freundlich isotherms.

Furthermore, values of $1/n$ were between zero and one, which indicates that Algerian MMT is favourable for the adsorption of MO

dye under the experimental conditions employed [24]. The comparison of adsorption capacities of various materials is given in Table 6.

Reference

- Annadurai G, Ling LY, Lee JF (2008) Adsorption of reactive dye from an aqueous solution by chitosan: isotherm, kinetic and thermodynamic analysis. *J Hazard Mater* 152: 337-346.
- Salleh MAM, Mahmoud DK, Karin WA, Idris A (2011) Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. *Desalination* 280: 1-13.
- Shi B, Li G, Wang D, Feng C, Tang H (2007) Removal of direct dyes by coagulation: the performance of preformed polymeric aluminum species. *J Hazard Mater* 143: 567-574.
- Nkurunziza T, Nduwayezu JB, Banadda EN, Nhapi I (2009) The effect of turbidity levels and *Moringa oleifera* concentration on the effectiveness of coagulation in water treatment. *Water Sci Technol* 59: 1551-1558.
- Khenifi A, Sekrane F, Kameche M, Deriche Z (2007) Adsorption study of an industrial dye by organic clay. *Adsorption* 13: 149-158.
- Chen S, Zhang J, Zhang C, Yue Q, Li Y, et al. (2010) Equilibrium and kinetic studies of methyl orange and methyl violet adsorption on activated carbon derived from *Phragmites australis*. *Desalination* 252: 149-156.
- Robinson T, Chandran B, Nigam P (2002) Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk. *Environ Int* 28: 29-33.
- Grses A, DoAYar C, YalAin M, Aikyildiz M, Bayrak R, et al. (2006) The adsorption kinetics of the cationic dye, methylene blue, onto clay. *J Hazard Mater* 131: 217-228.
- Medjdoub L, Rahmouni A, Belbachir M (2014) New approach for synthesis of hexa (allylamino) cyclotriphosphazene catalysed by an ecologically friendly catalyst called Maghnite-H⁺ derived from Algerian MMT 2: 046-053.
- Ferrahi MI, Belbachir M (2005) Synthesis of cyclic polyesters of poly (oxybutylene oxymaleoyl). *J Polym Res* 12: 167-171.
- Ismail MA, Eltayeb MAZ, Abdel Maged SA (2013) Elimination of Heavy Metals from Aqueous Solutions using Zeolite LTA Synthesized from Sudanese Clay 3: 93-98.
- Wibulswas R (2004) Batch and fixed bed sorption of methylene blue on precursor and QUACs modified montmorillonite. *Sep Purif Technol* 39: 3-12.
- Almeida CA, Debacher NA, Downs AJ, Cottet L, Mello CA (2009) Removal of methylene blue from colored effluents by adsorption on montmorillonite clay. *J Colloid Interface Sci* 332: 46-53.
- DoÄYan M, Alkan M, TÄrkyilmaz A, Ozdemir Y (2004) Kinetics and mechanism of removal of methylene blue by adsorption onto perlite. *J Hazard Mater* 109: 141-148.
- Ho YS, Chiang CC, Hsu YC (2001) Sorption kinetics for dye removal from aqueous solution using activated clay. *Separation Science and Technology* 36: 2473-2488.
- Ferrero F (2010) Adsorption of Methylene Blue on magnesium silicate: kinetics, equilibria and comparison with other adsorbents. *J Environ Sci (China)* 22: 467-473.
- Tahir SS, Rauf N (2006) Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay. *Chemosphere* 63: 1842-1848.
- Benguella B, Yacouta-Nour A (2009) elimination des colorants acides en solution aqueuse par la bentonite et le kaolin. *CR Chimie* 12: 762-771.
- Bhakta JN, Muneke Y (2013) Identification of potential soil adsorbent for the removal of hazardous metals from aqueous phase. *Int J Environ Sci Technol* 10: 315-324.
- Fil BA, Yilmaz MT, Bayar S, Elkoca MT (2014) Investigation of adsorption of the dyestuff astrazon red violet 3rn (basic violet 16) on montmorillonite clay. *Braz J Chem Eng* 33: 171-182.
- ElOuardi M, Said A, Samir Q, Abdelhadi A, Ali A, et al. (2013) Removal of Carbaryl Pesticide from Aqueous Solution by Adsorption on Local Clay in Agadir. *American Journal of Analytical Chemistry* 4: 72-79.
- Tsai WTY, Chang YM, Lai CW, Lo CC (2005) Adsorption of Basic Dyes in Aqueous Solution by Clay Ad- sorbent from Regenerated Bleaching Earth. *Applied Clay Science* 29: 149-154.
- Venkat SM, Indra DM, Vimal CS (2007) Use of Bagasse Fly Ash as an Adsorbent for the Removal of Brilliant Green Dye from Aqueous Solution. *Dyes Pigments* 73: 269-278.
- Zhu L (2008) efficient removal and mechanisms of water soluble aromatic contaminants by a reduced-charge bentonite modified with benzyl tri methyl ammonium cation. *Chemosphere* 70: 1987-1994.