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Sorption of Methyl Orange from Aqueous Solution on Chitosan Biomass

Fella-Naouel Allouche[a*], Nouredine Yassaa[b], Hakim Lounici[c*]

[a]*Bioenergy and Environment Laboratory, Centre de Développement des Energies Renouvelables, B.P. 62, Route de l'Observatoire, Bouzaréah, 16340-Alger, Algeria.*

[b]*Centre de Développement des Energies Renouvelables, B.P. 62, Route de l'Observatoire, Bouzaréah, 16340-Alger, Algeria. n.yassaa@cder.dz.*

[c]*Ecole Nationale Polytechnique d'Alger, Laboratoire des Biotechnologies Environnementales et Génie des Procédés, 10, Hacen Badi, El Harrach-Alger, Algeria.*

Abstract

Many industries such as textile, pulp and paper, dyestuffs and plastics industries use dyes to color their products and discharge a considerable amount of colored wastewater into the environment. Dyes are recalcitrant molecules (particularly azo dyes), toxic and even carcinogenic and make a serious hazard to aquatic organisms. Therefore, it is necessary to eliminate them before discharging. This study investigates the adsorption behavior of Methyl orange (MO) from aqueous solution on chitosan biomass. In a preliminary study, the sorption of MO has been carried out as a function of shaking time, pH, dye concentration and temperature. The sorption of MO was characterized using SEM-EDAX and FT-IR spectroscopy. The equilibrium data on the Methyl orange fitted to both Langmuir and Freundlich isotherms, but the experimental data of the MO were found to be better fitted by the Freundlich model. Maximum sorption capacity reached up to 29 mg g^{-1} at pH 3 was achieved within 60 min. The sorption data were best fit with the pseudo-second-order kinetic model. These results indicate that chitosan is an interesting alternative for dye removal from the wastewater.

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Keywords: Chitosan; Methyl orange; sorption; isotherm; modeling.

* Corresponding author. Tel.: +213(0)21901503; fax: +213(0)21901560.
E-mail address: allouchenaouel2000@yahoo.fr

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1. INTRODUCTION

Industrial sectors like (textiles, plastics industry, paper industry, tanning) are large consumers of water and use soluble synthetic dyes or pigments to color their products. Their presence in water in trace amounts is undesirable even if the color is generally not toxic. The removal of color from a process or waste effluents becomes environmentally important. Today in Algeria, about 60% of wastewater is treated. This rate will be around 90% in 2015 at the completion of more water treatement programs. The management of water resources and water conservation has set a goal of "zero discharge of sewage at sea and in the wadis". Several methods have been developed for the treatment of wastewater contaminated with dyes such as photocatalytic degradation, electrochemical degradation, cation exchange membranes, biological treatment etc. Crini and Badot (2008). Adsorption processes are considered as an alternative for the treatment of colored wastewater. Most research has been conducted to find an alternative low cost adsorbents than conventional adsorbents (activated carbon (AC)), commercial resins) whose performance may vary from one material to the other. For example, activated carbon (AC) is very effective for acid and basic dyes but ineffective for dispersed dyes or metalliferous. On the other hand, clays can adsorb effectively basic dyes; also peat is particularly efficient for bleaching solutions containing cationic dyes, but it is lowest for acidic dyes. There is no known material to remove all types of dyes. Compared to conventional adsorbents, materials based on chitosan have a number of advantages (Crini et al., 2009; Rinaudo, 2006). This is an ecologically interesting product that has a specific chemical structure and is polycationic from natural polymers. Also chitosan is a biopolymer, which is among the most abundant polysaccharides in nature after cellulose, commercially extracted from the shells of crustaceans. This biodegradable and biocompatible biopolymer is interesting because of its wide range of applications (Kumar, 2000). One of the most important applications is based on its ability to strongly adsorb a wide range of pollutants, including dyes molecules.

The objective of this paper is to identify the main parameters controlling the fixation of methyl orange by chitosan (Fig. 1). The study of adsorption properties of chitosan through the determination of operating parameters such as the effect of pH, the adsorption isotherm (effect of pH, concentration of the dye). The approach will focus on the study of adsorption phenomena on chitosan through two types of experiments: kinetics and isotherms on batch method. Finally, a characterization study of chitosan by Fourier transform infrared spectroscopy (IFTR) and scanning electron microscope (SEM) before and after adsorption were carried out.

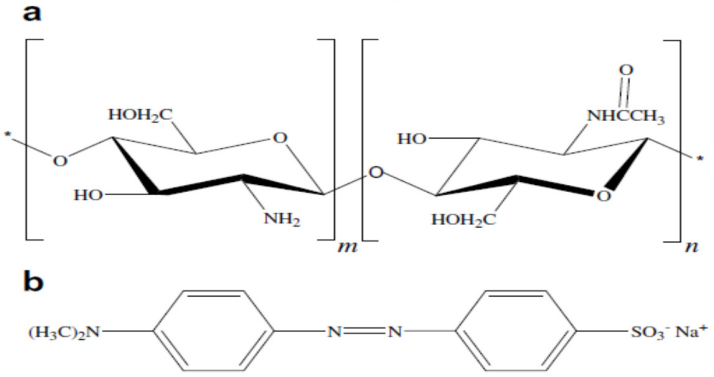

Fig. 1. Chemical structures of chitosan (a) methyl orange (b).

2. Experimental procedure

2.1. Materials

The chitosan used is supplied by the Aber Society (Plouvien, France). It is obtained from the crustacean shells chitin extraction and it is presented in a raw state as a 1-5 mm size flakes. It is characterized by an average deacetylation rate near 87% and an average molecular weight (M_W) was about 125000 g mol^{-1} (Guibal et al, 1998). The biosorbents used for sorption are obtained by grinding (JK Crusher, IKA Labortechnik Universal mühle M20) and sieving (sieve Stainless OSI NFX 11504) according to the particle size distribution repartition. Analytical grade

methyl orange (C14H14N3NaO3S; molecular weight 327.33) was obtained from Merck and was used as received. The dye solution was prepared at the desired concentration using distilled water.

2.2. Batch adsorption experiments

Adsorption measurements on chitosan were carried out in batch process. A desired amount of the adsorbent was added to 100 mL of the MO solution (various concentrations). The desired pH was achieved by adjustment with 0.1M HCl or 0.1M NaOH. The mixture was stirred magnetically at room temperature and 200 rpm, and samples were collected from the experimental flask at pre-determined time intervals until the adsorption equilibrium was reached. The dye solution was separated from the adsorbent by centrifugation at 10,000 rpm for 20 min and the residual dye concentrations in the solutions and measured using UV–vis spectrophotometer. All experiments were carried out in duplicate.

2.3. Adsorption capacity measurement

The analysis of concentration of MO was carried out by measuring of the absorbance of MO at 460 nm by using a UV spectrometer (Model Biomate UV/Vis- Spectrophotometer) absorbance maximum (460 nm). A calibration curve was plotted between the absorbance and the concentration of the MO solution to obtain the absorbance–concentration profile. The amount of MO uptake per unit of adsorbent (q) was calculated using the following equations:

$$q\_e = \mathrm{V(C\_(0\ ) - C\_(e\ ))/M}$$

where Ci is the initial MO concentration (mg L^{-1}), Ce is the MO concentration at the adsorption equilibrium (mg L^{-1}), V is the volume of MO solution (L), and m is the weight of the chitosan (g). The concentration of residual dye in the solution was determined by UV-spectrophotometry.

2.4. Material characterization

Samples of chitosan (fraction G2) characterized by Environmental Scanning Electron Microscope (ESEM) Quanta FEG 200. The morphology, porosity, particle size and surface roughness of the chitosan were analyzed. FTIR spectra were obtained using a (SHIMADZU 8400S) spectrometer.

3. Results and discussion

3.1. Characteristics of the adsorbent material

- Fourier Transform Infrared Spectroscopy

Chitosan, a natural linear copolymer that is primarily composed of β (1→4) linked 2-amino-2-deoxy-d-glucopyranose units, and residual 2-acetamido-2-deoxy-d-glucopyranose units, is a chemical derivative obtained by alkaline deacetylation of chitin and is also found naturally in some fungal cell walls. Chitosan has drawn particular attention as effective biosorbent due to its high contents of amino and hydroxyl functional groups showing high adsorption potential for various pollutants. FT-IR spectra for chitosan were recorded before and after MO biosorption (Fig.2). The large and intense bands located at 3000 and 3700 cm^{-1} can be attributed to axial OH and NH group vibrations, which are most evident in the chitosan spectra before sorption. On the other hand, the absorption band at 3480 cm^{-1} can be assigned to the hydrogen bond between OH on carbon-5 of the biopolymer structure with the carbonyl acetamide group. The main differences can be observed (a) in the range 1000-1600 cm^{-1} where the width of the broadband is reduced (sharper and more decided edge), at (b) 1384 cm-1 where the peak is less pronounced, and (a) to 1119 cm^{-1} and 1636 cm^{-1} , where the peaks are slightly reduced. This hints at amine / amide involvement with the functional groups of chitosan.

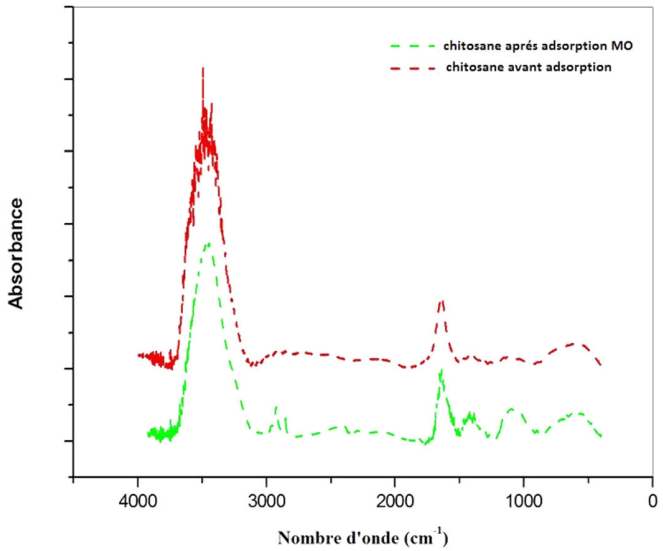

Fig. 2. FTIR Spectra of (A) chitosan before (a) and after (b) (MO) sorption.

- Scanning electron microscopy (SEM)

Chitosan were observed by scanning electron microscope. The results show that raw chitosan has a smooth surface and irregular morphology, Fig. 3 a) and 3 b). The chitosan used in this study has a homogeneous and uniform structure. The microscope observation confirms the presence of macrospore. Fig 3. shows the SEM-EDAX analysis before and after adsorption of methyl orange (MO). It can be seen after adsorption of methyl orange (MO) that chitosan is totally embedded in the surface.

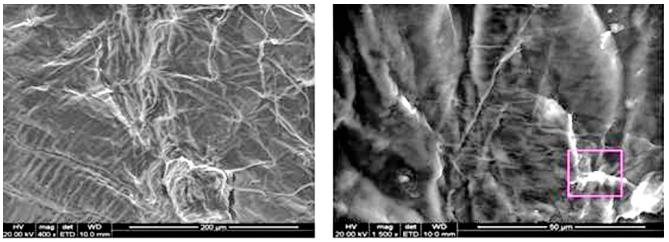

Fig. 3. SEM images for chitosan:
(a) before adsorption (200 µm) ; (b) chitosan after adsorption of MO (50 µm).

3.2. Adsorption studies

The equilibrium adsorption isotherm of methyl orange from an aqueous solution using chitosan powder was investigated in batch. In this study, two models commonly used, the Freundlich (1906) and Langmuir (1916) isotherm, were applied to understand the dye–chitosan interaction. The Langmuir isotherm is based on the assumption of monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption. The Freundlich isotherm describes a heterogeneous system and reversible adsorption and is not restricted to monolayer formation. The Langmuir adsorption model is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The equation is given as:

$$q_e = \mathrm{q_m b\ C_e} / 1 + \mathrm{b\ C_e} \quad (1)$$

In Eq. (1), q_e represents the concentration at equilibrium in the solid. q_m is the maximum amount of adsorption or Langmuir monolayer sorption capacity (mg g^{-1}); b is the Langmuir constant, (L mg^{-1}); C_e is the equilibrium

concentration of metal in solution, (mg L^{-1}) where q_m and b are the monolayer maximum adsorption capacity at saturation and the constant equilibrium adsorption indicating the affinity between the solid and the adsorbent, respectively. The parameter q_m and b are calculated from the slopes and intercept behind the lines was mathematically expressed by linearized (Equation 3):

$$\frac{1}{q_e} = 1/q_m + 1/q_m b C_e \quad (2)$$

The Langmuir constants K_L and q_m can be determined from the intercept and slope of the linear plot of 1/qe versus 1/Ce (Fig 4.) and are presented in Table 1.

Table 1. Isotherm parameters for adsorption of methyl orange on chitosan

	Langmuir parameters		
pH	**qm (mg MO g^{-1})**	**b (L mg^{-1})**	**R^2**
3	29	0.025	0.992

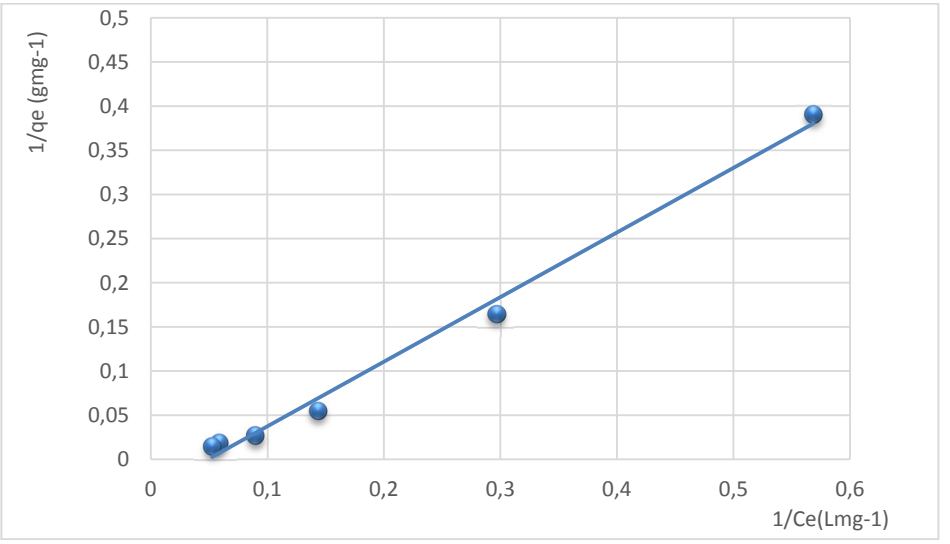

Fig. 4. Langmuir models for MO adsorption onto chitosan at pH 3

Figure 4 represents the equilibrium dye isotherm of Methyl Orange (MO) on chitosan. After dye adsorption, the adsorption equilibrium qe increases with increasing of dye ceoncentration. It can be seen that the Langmuir model was obviously the most appropriate to describe the adsorption process due to its high correlation coefficients relative to the ones obtained from Freundlich model.

Chitosan is fully protonated at around pH 3.0; various kinds of dyes are studied. Dotto et Pinto, (2011) studied the adsorption of different acid dyes onto chitosan such as Acid bleu 9 and Yellow 3. Iqbal et al., (2011) worked on the biosorption of Acid yellow 73, Wong et al., 2004 on biosorption Acid orange 10 and 12, acid green 25, acid red 18 and 73 respectively. The adsorption capacities on azo dyes are investigated. Table. 2 lists a comparison of the maximum adsorption capacities (qmax) of MO on various adsorbents. Calcined Lapindo volcanic mud CLVM has a relatively large adsorption capacity (333.33 $mgMOg^{-1}$), suggesting that it may be a promising material for removal of azo dyes from aqueous solutions Jalil et al, (2010), 238.1 mg MOg^{-1} by activated carbon Chen et al. (2010). Adsorption capacities between 10 and 20 mg MOg^{-1} were obtained using activated alumina Iida et al, (2004) and

Banana peel Gurusamy et al, (2002). In this study, the biosorption capacity of chitosan presents an intermediate values between the modified chitosan and chitosan beads (Huang et al., 2008). Despite this results, chitosan remains competitive compared to others conventional adsorbents.

Table 2. Comparison maximum adsorption capacities of various adsorbents for methyl orange (MO).

Biosorbant	pH	Spécifiques expérimentales conditions	qm ou qmax (mg MO g^{-1})	References
Chitosan beads	5		7,2	Morais et al, (2008)
	7		5,8	
	8		5,6	
Calcined Lapindo volcanic mud		40°C	333,33	Jalil et al, (2010)
Activated alumina	3-6	20°C	9.8	Iida et al, (2004)
Banana peel	5,7	30°C	21	Gurusamy et al, (2002)
Modified chitosane			89,30	Huang et a, (2013)
Activated carbon *Phragmites australis*	-	10°C	238.1	Chen et al, (2010)
Chitosan	3	25°C	29	*This study*

4. Conclusion

Chitosan represents an attractive alternative to other biomaterials, mainly because of its physico-chemical characteristics, chemical stability and biodegradability. The present study investigated the adsorption of MO from aqueous solutions by chitosan. The Langmuir equation agreed with the equilibrium isotherm for all the cases studied. The maximum monolayer adsorption capacities obtained from the Langmuir model was 29 mg/g at 25°C. With these results, we conclude that chitosan is an eco-friendly adsorbent for dye removal at low concentration of colored wastewater and industrial effluents.

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