Desalination and Water Treatment
www.deswater.com

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doi: 10/5004/dwt.2012.3354

39(2012)316–322
February

Removal of organic pollutants from industrial wastewater: performance evaluation of inorganic adsorbents based on pillared clays

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Received 29 November 2010; Accepted 4 April 2011

ABSTRACT

This work reports the application of a natural clay and an alumina-pillared clay as adsorbents for the removal of a basic dye, Methylene Blue, from aqueous solutions. The intercalation and pillaring processes improve the adsorption capacity of the montmorillonite. The adsorption kinetics of the dye has been studied in terms of pseudo-first-order and pseudo-second-order models. The equilibrium data are mathematically modelled using Freundlich, Langmuir and Sips isotherm adsorption models.

Keywords: Pillared clay adsorbents; Methylene blue; Dyes adsorption; Wastewaters; Organic pollutants; Kinetics and equilibrium adsorption modeling

1. Introduction

The quality of industrial effluents has a substantial influence on the quality of surface water. Most industrial effluents require treatment before their direct discharge into surface waters or their delivery to municipal treatment plants. There are numerous industries that consume large volumes of water and use organic chemicals: textile, paper and pulp, printing, iron-steel, coke, petroleum, pesticide, paint, solvent, pharmaceutics, wood preserving chemical or food industry are some examples. Pollutants from these industries can be a serious problem to the environment and to the human health [1].

Textile industries in particular are responsible for the discharge of dyes into natural waterways due to inefficiencies in dyeing techniques: when reactive dyes are used, up to 50% may be lost directly into waterways. The presence of dyes, even at very low concentrations, is highly visible and undesirable in an effluent. In addition, some dyes are toxic, mutagenic or carcinogenic [2].

Adsorption is an attractive method for the removal of contaminants from effluents since if the adsorption system is designed correctly; it will produce a high-quality treated effluent [3]. The adsorption process, in comparison with other processes for the treatment of polluted aqueous effluents, allows flexibility in design and operation, and produces effluents suitable for reuse, free of pollutants [4]. Additionally, as the adsorption is sometimes reversible, the regeneration of the sorbent with resultant economy of operation can be possible.

Interesting opportunities in the field of the synthesis and applications of clay-based materials have been

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3rd International Conference on Small and Decentralized Water and Wastewater Treatment Plants (SWAT-III), Skiathos, Greece, 14–16 May 2010

opened with the development of pillared interlayered clays, in short PILCs [5,6]. The structure of PILCs is simple. Their pore network consists of rigid polycations inserted among the clay layers, resulting to a two-dimensional porous structure of molecular dimensions. The chemical nature of the surface of PILCs is more complex. Their properties depend on many factors, as the clay nature and the intercalation and pillaring steps [6].

The aim of this work is to study the performance of a montmorillonite and an alumina pillared clay as adsorbents of Methylene Blue from aqueous solutions. To this end, various kinetics and equilibrium models are applied to the experimental data of adsorption.

2. Experimental

2.1. Preparation of the adsorbents

The purified natural clay mineral used in this work was a montmorillonite from Tsukinuno, supplied by *The Clay Science Society of Japan*. The clay was intercalated with aluminium hydroxyl-polycations following a standard procedure [7]. The aluminium hydroxyl-polycation solution [8,9] has been prepared by slow addition of a 1.5 mol/dm^3 solution of NaOH (Aldrich, 97%) to a 0.5 mol/dm^3 solution of $AlCl_3$ $6H_2O$ (Merck, 97%) under vigorous stirring, with an OH^-/Al^{3+} mole ratio equal to 2. The hydrolysed solution was allowed to age for 48 h at 323 K under continuous stirring. An Al/clay ratio of 10 $mmol_{Al}/dm^3 \cdot g_{clay}$ was used in the intercalation process. The clay suspensions were kept in contact with the solution for 24 h at room temperature, washed by centrifugation, dried for 16 h at 373 K. The solids are designated hereafter as *Tsu-Mont* and *Al-PILC*, which refers to the Tsukinuno montmorillonite used in the intercalation process and to the pillared montmorillonite.

2.2. Characterization of clays

Textural analyses were carried out from the corresponding nitrogen (Air Liquide, 99.999%) adsorption at 77 K, obtained from a static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyser). 0.1 g of the samples were degassed for 24 h at 473 K at a pressure lower than 0.133 Pa.

2.3. Adsorption experiments

For all adsorption experiments, the concentration of Methylene Blue (Merck, Basic blue 9, $C_{16}H_{18}ClN_3S$) in the supernatant was determined by UV-visible spectroscopy at the wavelength of 660 nm. A Hewlett-Packard 8453, Diode Array UV-vis spectrophotometer was used for these analyses.

To measure the adsorption kinetics of the dye onto the clays, 10 cm^3 of a Methylene Blue solution with an initial concentration in the range of 150–800 ppm was introduced into the glass vials and mixed with 0.1 g of the adsorbents. The suspension was stirred continuously at room temperature and the pH was maintained at a value of 5.0 ± 0.3. At pre-determined time intervals between 0.5 and 40 min, the solutions were separated from the adsorbent by centrifugation for 10 min at 3500 r.p.m. and the dye concentration in the supernatant was determined. The amount of dye adsorbed on clay was calculated as the change in the aqueous-phase concentration from the initial value, according to the following equation:

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \tag{1}$$

where C_0 = the initial concentration (mg/dm^3); C_t is the concentration (mg/dm^3) at a certain adsorption time t (min), V is the solution volume (dm^3); and m is the amount of clay (g).

Several solutions of Methylene Blue with various concentrations were prepared in order to determine the equilibrium adsorption capacity of the two clay mineral samples. Typically, 0.1 g of the adsorbent was poured into the glass vials with 10 cm^3 of the dye solutions, ranging from 50 to 700 mg/dm^3, and the mix was kept under constant stirring for the time determined in the previous procedure to reach the equilibrium. The pH was maintained at a value of 5.0 ± 0.3. The solutions were separated from the adsorbent by centrifugation for 10 min at 3500 r.p.m. and the dye concentration in the supernatant was determined. The amount of dye adsorbed on clay was calculated as the change in the aqueous-phase concentration from the initial value, according to the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{2}$$

where C_0 = the initial concentration (mg/dm^3); C_e = the equilibrium concentration (mg/dm^3); V = the solution volume (dm^3); and m = the amount of clay (g).

3. Theoretical approach

3.1. Kinetic modeling

Several isotherm equations have been proposed to describe the experimental data from adsorption procedures [10]. The models that show how the q_t changes with the adsorption time are simple and easy to apply for practical operations. Some models in this category are: the pseudo-first-order and the pseudo-second-order rate equations.

In first order decay, the amount of material decaying in a given period of time is directly proportional to the amount of material remaining. The first-order rate equation or the so-called Langergren equation is commonly expressed as Eq. (3) [11]. The first-order rate equation indeed is in line with the concept of linear driving force.

$$\frac{\mathrm{d}\,q}{\mathrm{d}\,t} = k_1 \cdot \left(q_e - q\right) \tag{3}$$

which can be integrated for boundary conditions ($t = 0 - t$ and $q = 0 - q_t$), leading to:

$$q_t = q_e \cdot [1 - \exp(-k_1 \cdot t)] \tag{4}$$

where k_1 (1/min) = the first order rate constant; q_t (mg/g) = the amount of adsorbate adsorbed at time t (min); and q_e (mg/g) = its value at equilibrium.

The second-order rate equation was first proposed by Blanchard et al. [12], and it has been frequently employed to analyse adsorption data obtained from various experiments with several types of adsorbates and adsorbents as reviewed by Ho et al. [13]:

$$\frac{\mathrm{d}\,q}{\mathrm{d}\,t} = k_2 \cdot \left(q_e - q\right)^2 \tag{5}$$

which can be integrated for boundary conditions ($t = 0 - t$ and $q = 0 - q_t$), leading to:

$$q_t = \frac{k_2 \cdot q_e \cdot t}{1 + k_2 \cdot q_e \cdot t} \tag{6}$$

where k_2 (g·mg/min) = the rate constant of the pseudo-second-order adsorption; q_t (mg/g) = the amount of adsorbate adsorbed at time t (min); and q_e (mg/g) is its value at equilibrium.

According to Liu and Shen in nearly all kinetic studies of adsorption, both first- and second-order rate equations have been commonly employed in parallel, and one is often claimed to be better than another according to a marginal difference in correlation coefficient [11].

3.2. Equilibrium modeling

The most common representation of the adsorbate concentration and quantity of material adsorbed is the adsorption isotherm. The equilibrium adsorption isotherm is fundamental in describing the interactive behaviour between solutes and adsorbent, and is important for the design of the adsorption system [14]. In this study the Langmuir, Freundlich and Sips isotherms equations were used for modeling of experimental data.

3.2.1. Langmuir equation

Langmuir suggested a theory to describe the monolayer coverage of adsorbate over a homogeneous adsorbent surface. The adsorption isotherm is based on the assumption that sorption takes place at specific homogeneous sites within the adsorbent. Once an adsorbent molecule occupies a site, no further adsorption can take place at that site [15]. Thus, an equilibrium value can be reached and the saturated monolayer curve can be expressed as:

$$q_e = \frac{q_L \cdot k_L \cdot C_e}{1 + k_L \cdot C_e} \tag{7}$$

where q_e (mg/g) = the solid phase concentration of adsorbed species at equilibrium; C_e (mg/dm^3) = the equilibrium concentration of the adsorbate in the solution at equilibrium; q_L (mg/g) and k_L (dm^3/mg) = Langmuir constants, which represent the monolayer adsorption capacity and the adsorption energy.

3.2.2. Freundlich equation

In 1906, Freundlich suggested a model to describe the properties of heterogeneous systems [16]. This model has been widely applied in heterogeneous adsorption systems especially for organic compounds and high interactive species on activated carbon. The studies from Freundlich showed that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solution was not a constant at different solution concentrations; the author proposed this multi-site adsorption isotherm for heterogeneous surfaces [15]. The Freundlich isotherm equation can be expressed as follows:

$$q_e = k_F \cdot C_e^{1/m_F} \tag{8}$$

where q_e (mg/g) = the solid phase concentration of adsorbed species at equilibrium; C_e (mg/dm^3) = the equilibrium concentration of the adsorbate in the solution at equilibrium; k_F and m_F = empirical constants and indicate the adsorption magnitude and effectiveness.

3.2.3. Sips equation

The model is a combination of the Langmuir and Freundlich isotherm type models. At low sorbate concentrations it effectively reduces to a Freundlich isotherm, while at high sorbate concentrations it predicts a monolayer adsorption capacity characteristic of the

Langmuir isotherm [17]. The Sips equation isotherm can be expressed as:

$$q_e = \frac{q_S \cdot k_S \cdot C_e^{m_S}}{1 + k_S \cdot C_e^{m_S}} \tag{9}$$

where q_e (mg/g) = the solid phase concentration of adsorbed species at equilibrium; C_e (mg/dm^3) = the equilibrium concentration of the adsorbate in the solution at equilibrium; q_S (mg/g) and k_S (cm^3/mg) = the Sips constants and they represent the monolayer adsorption capacity and the adsorption energy, respectively; m_S is an empirical constant.

4. Results and discussion

4.1. Characterization of the clays

The textural properties of the clays were summarized in Table 1, indicating that the intercalation and pillaring processes produced an important increase of the surface area and pore volume in comparison with the montmorillonite. The Langmuir surface area (S_{Lang}) was calculated from adsorption data over the relative pressure rang between 0.01 and 0.05, taking the cross-sectional area of the nitrogen molecule as 0.162 nm^2 [18]. The total pore volume (V_p) was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99, assuming the density of the nitrogen condensed in the pores is equal to that of liquid nitrogen at 77 K (0.81 g/cm^3) [18]. The external surface area (S_{ext}) and the micropore volume ($V_{\mu p}$) have been estimated by the t-plot method [18].

The pillared clay of this work exhibit high specific surface area, reaching a value of 406 m^2/g, value higher than that of the natural clay, 9 m^2/g. An important increase of the volume adsorbed by the micropores takes place as a result of the pillaring process, from 0.002 cm^3/g for the natural clay to 0.149 cm^3/g for the Al-PILC (see Table 1). The mesoporous region was characterized using the Barrett–Joyner–Halenda (BJH) method [19]. The comparisons of the mesopore volumes (V_{mp}) for pores in the range of 1.5–50 nm, as determined by the BJH analysis, are also given in Table 1. The pillaring process does not influence the mesopore size range. An increase of the external surface area with the pillaring process is also observed.

Table 1
Specific surface areas and pore volumes of the adsorbents

	S_{Lang} (m^2/g)	S_{ext} (m^2/g)	V_p (cm^3/g)	$V_{\mu p}$ (cm^3/g)	V_{mp} (cm^3/g)
Tsu-Mont	9	3	0.047	0.002	0.020
Al-PILC	406	13	0.185	0.149	0.027

4.2. Adsorption experiments

The adsorption of pollutants from aqueous solutions plays a significant role in water pollution control. It is therefore important to be able to predict the rate at which the contaminant is removed from aqueous solutions in order to design an appropriate adsorption treatment plant [20].

The evaluation of the amount of adsorbed Methylene Blue, q_t, as a function of the adsorption time is presented in Fig. 1. The adsorption kinetics parameters are estimated by non-linear regression and the values are listed in Table 2. The adsorption kinetics for the two clays does not show a significant difference. However, the pillared clay has a higher adsorption capacity than the montmorillonite. It can be related to the pillaring process which results in materials with altered chemical composition, surface acidity and structure. In particular, surface areas and pore volumes are significantly increased following pillaring processes [21].

It seems that the effect of the adsorbate concentration is an interesting parameter to be considered in the kinetics experiments [20,22]. The results show that the amount of Methylene Blue adsorbed at equilibrium increases with an increase in initial adsorbate concentration. The increase in the initial dye concentration from 150 to 800 ppm causes an increasing in the removal of dye from 13 to 30 mg/g and from 15 to 70 mg/g for Tsu-Mont and Al-PILC, respectively. It can also be observed that at 150 ppm concentration there is a faster increase in the amount of dye adsorbed at the beginning of the experiment. At 800 ppm concentration, the system needs more time to reach the equilibrium concentration. A similar effect has been observed in a study of copper (II) sorption by chitosan [23]. At low initial adsorbate concentration, the adsorbate will bind preferentially to high-energy sites. The sites of higher energy are usually taken up by adsorbate molecules first, with sites of lower energy progressively filled as adsorbate loading is increased. It follows that the adsorbate bond in low adsorbate loading situations will result in faster reaction kinetics, as it is possible to see by the high values of k_2 (see Table 2). Adsorption on sites of lower energy, as in the case of high loading, will subsequently result in a decrease in the k_2 value (see also Table 2).

The adsorption equilibrium data were fitted to the Freundlich, Langmuir and Sips isotherm models. Each model constants are used for predicting the adsorption capacities and also for incorporating into mass transfer relationship to predict the design of contacting experiments [24]. The experimental data and the three modelled isotherms are presented in Fig. 2. The best fitting results were obtained with the Sips isotherm model, therefore this isotherm is the one selected to be presented together with the experimental data in Fig. 2. The parameters were

Table 2
Pseudo-first and pseudo-second-order rate parameters for the Methylene Blue adsorption by Tsu-Mont and Al-PILC

	Tsu-Mont			Al-PILC		
	150 ppm	300 ppm	800 ppm	150 ppm	300 ppm	800 ppm
First-order						
k_1 (1/min)	1.66	0.58	0.80	1.03	0.60	0.32
χ^2	2	33	495	53	116	543
R	0.88	0.84	0.49	0.85	0.73	0.91
Second-order						
k_2 (mg/g·min)	0.556	0.047	0.061	0.136	0.045	0.008
χ^2	6	8	463	81	35	394
R	0.65	0.96	0.54	0.76	0.93	0.94

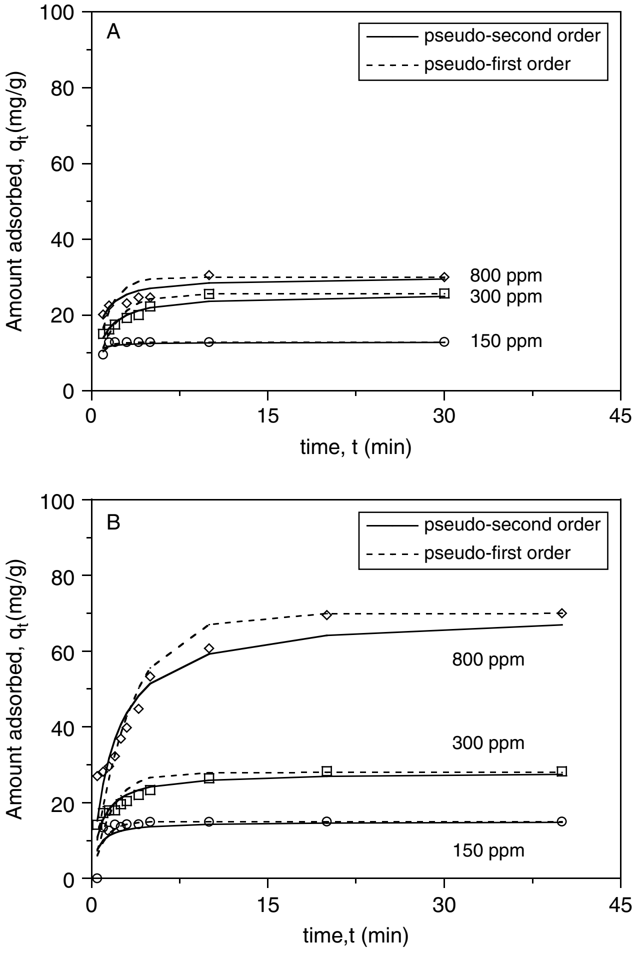

Fig. 1. Effect of the initial concentration on the adsorption of Methylene Blue on Tsu-Mont (a) and Al-PILC (b).

estimated by non-linear regression and the values are summarized in Table 3. For comparison, results obtained from the literature on Methylene Blue adsorption by several adsorbents are summarized in Table 4.

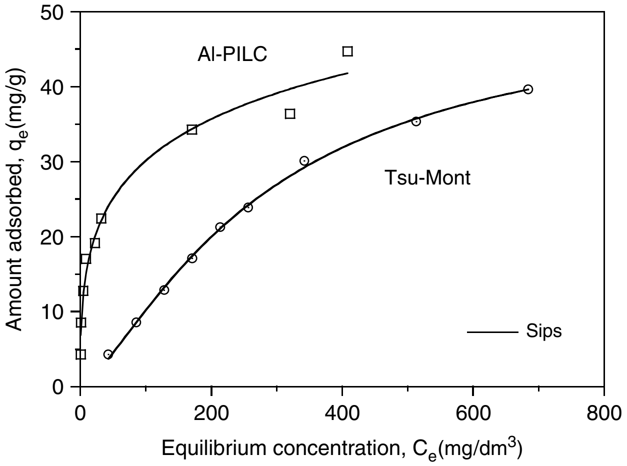

Fig. 2. Equilibrium adsorption data of Methylene Blue on Tsu-Mont and Al-PILC.

5. Summary and conclusions

In the present study, the removal of Methylene Blue from water solutions was investigated by using as adsorbents a natural Montmorillonite (Tsu-Mont) and its aluminium pillared form (Al-PILC). The kinetic studies showed that 10 min of agitation is sufficient to reach a complete equilibrium for the low-dye-concentration/clay system. The adsorption of Methylene Blue onto both clays obeyed pseudo-second-order kinetics. The best equilibrium adsorption isotherm fit was obtained with the Sips model, although Freundlich model had the same good behaviour in the Methylene Blue adsorption onto Al-PILC. The natural clay and its pillared form have a similar adsorption capacity. However, it is possible to verify that Al-PILC has a higher adsorption capacity, especially at initial concentrations of dye in the solution.

Table 3
Freundlich, Langmuir and Sips equation parameters for the Methylene Blue adsorption by Tsu-Mont and Al-PILC

	Tsu-Mont	Al-PILC
Freundlich		
k_F	0.60	8.20
m_F	1.5	3.7
χ^2	36	36
R	0.98	0.98
Langmuir		
q_L (mg/g)	73	40
k_L (dm^3/mg)	0.0018	0.061
χ^2	10	145
R	0.996	0.95
Sips		
q_S (mg/g)	51	97
k_S(dm^3/mg)	0.00046	0.082
m_S	1.4	0.4
χ^2	2	32
R	0.9993	0.98

Table 4
Adsorption capacity (q_e) of Methylene Blue and comparison with other adsorbents

Adsorbent	q_e (mg/g)	Reference
Activated Carbon F-400	409	[25]
Banana peels	181	[26]
Humic acid immobilized zirconium pillared montmorillonite	195	[27]
Kaolinite	77	[28]
Montmorillonite	110	[29]
Na-ghassoulite	135	[30]
Pansil	104	[31]
Peat	238	[32]
Sepiolite	110	[31]
Al-pillared clays	40–97	[This work]

Acknowledgements

Spanish authors gratefully thank the financial support from the Spanish Ministry of Science and Innovation (MICINN) and the European Regional Development Fund (FEDER) through projects MAT2007-66439-C02 and MAT2010-21177-C02-01. Brazilian authors gratefully acknowledge the financial support of the Brazilian Research funding agencies FAPESP, CNPQ and CAPES. F.C.C. Assis acknowledges financial support from Government of Navarra through a PhD fellowship.

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