

Removal of methylene blue from aqueous solution by fibrous clay minerals

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Received 26 July 2005; received in revised form 4 October 2005; accepted 16 November 2005

Available online 4 January 2006

Abstract

Kinetics and equilibrium processes of the methylene blue (MB) retention from aqueous solution by a mixture of fibrous clay minerals, which was isolated from a naturally occurring clay, were investigated. For these purposes, the effects of contact time, initial adsorbate concentration, adsorbent content, pH and ionic strength were determined. The results show that the MB retention obeys a pseudo-first order equation and the process is a diffusion controlled solid-state reaction. Moreover, the isotherm data fitted the Langmuir equation and the MB binding process became more energetic with the increase of the adsorbent concentration. In addition, the augmentation of the clay content or the initial MB concentration reduced the adsorption capacity, presumably because of the clay particles microaggregation and/or the occurrence of MB deriving species. On the other hand, it is observed that the MB uptake limit is reduced in low acid pH, particularly below the PZC, as well as in ionic strength solutions. These facts are linked to the silanol group protonation and to the reduction of the electrostatic forces induced by the clay particles, respectively.

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Keywords: Methylene blue; Fibrous clay minerals; Retention; Kinetics; Isotherms

1. Introduction

The presence of methylene blue (MB), an organic dye, in discharged water is hazardous for human beings and limits light diffusion and consequently the photosynthesis processes are reduced [1–3]. Activated carbon is suitable for removing minor amounts of such organic dyes from aqueous solutions. Unfortunately, this effective adsorbent is expensive and has high regeneration cost. For these reasons, different studies have been carried out in order to find out inexpensive adsorbing materials. Thus, the adsorption capacities of some clay minerals (e.g. [4–6]), agricultural residues (e.g. [7]) fly ash and mud [1,8] and other materials [9,10] were evaluated.

Because of their natural hollow brick-like structure, fibrous clay minerals namely palygorskite (ideal formula: $\text{Si}_8\text{Mg}_5\text{O}_{20}(\text{OH})_2(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$) and sepiolite (ideal formula: $\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$) have great potential for the retention of micro-pollutants such as heavy metals cations and

dyestuffs [11]. The cross-sections of the zeolite channels of palygorskite and sepiolite are $3.7 \text{ \AA} \times 6.4 \text{ \AA}$ and $3.7 \text{ \AA} \times 10.6 \text{ \AA}$.

If theoretical studies dealing with the adsorption of methylene blue onto sepiolite have been attempted [12], no attention is paid to the kinetics aspect of this process. Moreover, no systematic study is concerned with the effect of the operating conditions on MB fixation onto palygorskite. Thereby, this work is devoted to the kinetics and equilibrium studies of MB retention from aqueous solutions by fibrous clay minerals.

2. Materials and experimental procedures

The adsorbent is a clay fraction ($<2 \mu\text{m}$), which is isolated from a naturally occurring local clay [13] and Na-loaded according to the procedure described in reference [14]. It consists of a mixture of palygorskite (86 wt.%) and sepiolite (14 wt.%). The average length and width of the fibres turns around 2.7 and 0.03 μm , respectively. The cation-exchange capacity (CEC), determined as reported in reference [15], and the surface area (N_2 , BET) of the concerned clay fraction are 30 meq/100 g and 115 m^2/g respectively.

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The used methylene blue dye ($C_{16}H_{18}N_3SCl$) is a Merck product (95 wt.% of purity), which was oven-dried for 2 h at 110 °C. The UV–vis spectra of MB aqueous solutions displayed an intense band at 664 nm and a weak shoulder at around 605 nm.

For the kinetics study, suspensions of Na-saturated clay fraction were mixed to MB aqueous solutions in such a way that the clay content was kept constant (0.3 g/L) and the MB concentration was varied in the range 10–25 mg/L ($(3.5\text{--}8.8) \times 10^{-5}$ mol/L). The temperature, before and after the mix, was maintained at 298 K. The working pH was 4, since no appreciable pH evolution was observed in such condition. To determine the unretained MB amount, samples were taken from the mixture at regular contact time intervals and centrifuged at 10,000 rpm for 10 min. Then, the MB amount in the supernatant was determined from an experimental curve representing the absorbance of 664 nm radiation (measured by means of a UV–vis JASCO 7800 spectrophotometer) versus MB concentration. In this respect, it should be noticed that the Beer–Lambert law is followed for up to about 10 mg/L (3.5×10^{-5} mol/L). Thus, supernatants for which the initial MB concentration exceeds 10 mg/L were diluted, then analysed by spectrophotometry.

Concerning the equilibrium experiments, aqueous suspensions containing 5, 10 and 25 mg/L of Na-loaded clay fraction were mixed to MB solutions and shaken at constant temperature (298 K). After 24 h of contact, the supernatant was isolated by centrifugation, under isothermal condition, and the MB content was determined by UV–vis spectrometry, following the above procedure. The measured pH for the initial and equilibrium states is quasi constant (6.1).

3. Results and discussion

3.1. Kinetic study

Typical kinetic curves of MB fixation onto Na-saturated fibrous clay minerals are plotted in Fig. 1. An overall observation shows that the MB major amount was fixed in less than 5 min and the uptake limit was achieved in about 100 min. The

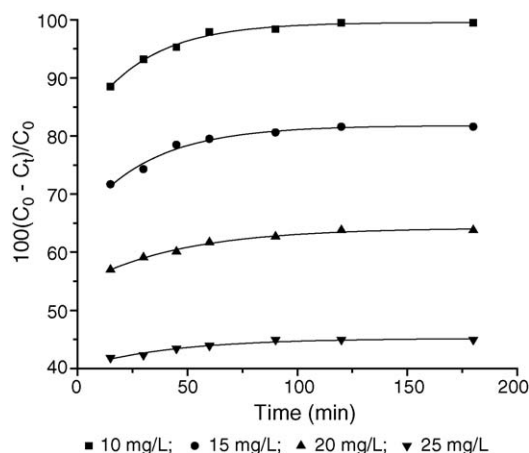


Fig. 1. Kinetic curves of the methylene blue retention by Na-saturated fibrous clay minerals. Initial MB concentrations: 10, 15, 20 and 25 mg/L; $T = 298$ K.

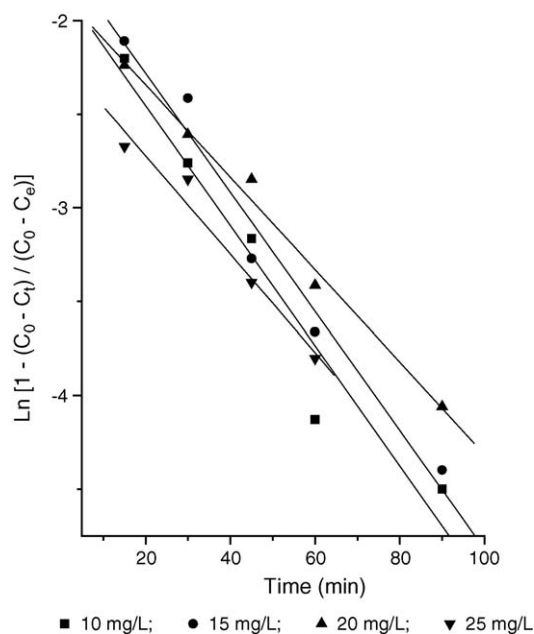
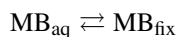


Fig. 2. Evolution of $\text{Ln}[1 - (C_0 - C_t)/(C_0 - C_e)]$ vs. time for different MB concentrations.

mathematical analyses of the kinetics data demonstrate that MB fixation obeys the pseudo-first reaction law (Fig. 2):

$$\text{Ln} \left[1 - \frac{C_0 - C_t}{C_0 - C_e} \right] = -k_c t$$

C_0 , C_t and C_e are the initial, instantaneous and equilibrium concentrations of MB^+ respectively, and k_c is the kinetic constant. The determined value of k_c is $(29 \pm 3)10^{-3} \text{ min}^{-1}$. In other respect, considering the MB equilibrium state:



(MB_{aq} and MB_{fix} are the free and clay-bonded MB species in solution), reached after an infinite time of MB–clay particles contact, the constant, K_d , for this partition process may be written as:

$$K_d = \frac{X_e/m}{C_e}$$

where X_e is the MB retained amount; $X_e = (C_0 - C_e)V_s$ (V_s is the volume of solution and m the clay content (0.3 g/L)). Given that the MB retention process was realized under isothermal condition, K_d should be constant. However, it is found that K_d declines with the initial MB concentration, according to the relation:

$$\frac{K_d - 1.67}{13.4} = \exp - \frac{C_0 - 15}{4.32}$$

This result may let to think that the free and fixed MB species are not alike. In fact, if the monomer is the main species occurring in MB solutions with less than about 7×10^{-6} M [15], the deriving MB ions such as dimmers, trimmers and/or protonated MB species are commonly formed in the contact of clay particle surfaces, and their relative proportions depend on the clay loading [5,16,17]. Taking for instance the solute concentrated solution ($C_0 = 25$ mg/L), the MB retained amount should

be 25 mg/L instead of 11.2 mg/L. Based on the fact that the amount of the available clay charged sites is 3×10^{-4} mol/g of clay and the MB retained amount is only 1.3×10^{-4} mol/g of clay, it appears that the major MB fixed species were present as MBH^{2+} . In contrast, the main fixed species for the diluted solution ($C_0 = 15$ mg/L) seems to be MB^+ .

One may also think that the above limited MB fixation is linked to a partial solute repulsion by clay particles because of the protonation of silanol groups (Si–OH), happened in acid pH. To evidence such eventual process, the MB retention versus time was followed in alkaline medium (pH 9). The corresponding result is not shown here. It is found that the distribution coefficient increased and the above kinetics law remained unchanged. This result suggests that supplementary active sites are developed in alkaline solution because of the deprotonation of Si–OH groups. As compared with the result of the run conducted in acid solution, the amount of the occurring sites, in alkaline pH, is estimated to be 7×10^{-4} mol/100 g. This is insignificant as compared with CEC. On the other hand, it is worth noting that pH of the alkaline solution declined as a function of the MB–clay contact time (Fig. 3), whereas a steady state is observed for pH acid medium. Thus, it may be concluded that BM fixation in alkaline condition is accompanied by the release of protons, deriving from the silanol groups.

For a deeper insight into the mechanism, which is behind the above K_d change, the actual and expected clay loadings versus the initial MB concentration was plotted. As can be deduced from Fig. 4 the uptake limit for $C_0 \geq 15$ mg/L is almost constant (40 ± 2 mg/g of clay). Apparently, only about the half of the clay permanent charged sites (P sites) is reached by MB^+ ions. This let to think that the MB fixation contributed to the formation of clay micro-agglomerates.

To determine the controlling factors of the MB retention kinetic, a mathematical analyses of the kinetics data was done

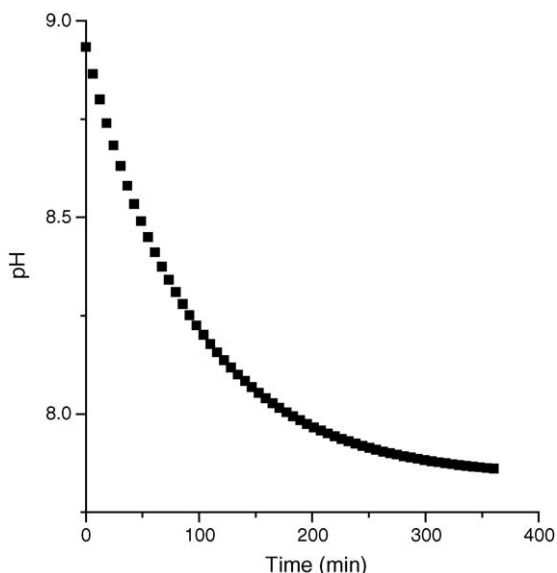


Fig. 3. Evolution of pH as a function of MB–clay contact time. Initial MB concentration: 15 mg/L; clay content: 0.3 g/L.

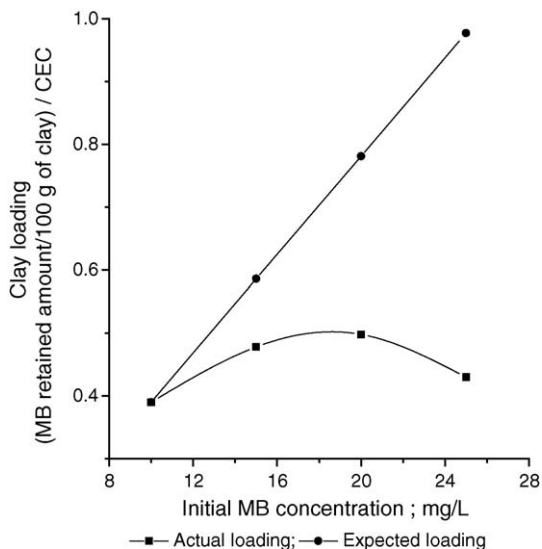


Fig. 4. Evolutions of actual and expected clay loadings a function of initial MB concentration.

on the basis of the following equation:

$$\frac{C_0 - C_t}{C_0 - C_e} = F(t) = 1 - \frac{6}{\pi^2} \exp\left(-\frac{\pi^2 Dt}{r^2}\right)$$

which derives from the second diffusion Fick’s law:

$$\frac{C_0 - C_t}{C_0 - C_e} = F(t) = 1 - \frac{6}{\pi^2} \sum_{n=2}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 Dt}{r^2}\right)$$

where $F(t) > 0.8$. The obtained result showed that $\ln[1 - F(t)]$ versus time manifests a linear evolution, as shown in Fig. 2, and consequently the MB retention process is a diffusion controlled solid-state reaction. The estimated diffusion coefficient for particles whose equivalent spherical radius (r) equals 10^{-6} m is 5×10^{-13} cm²/s.

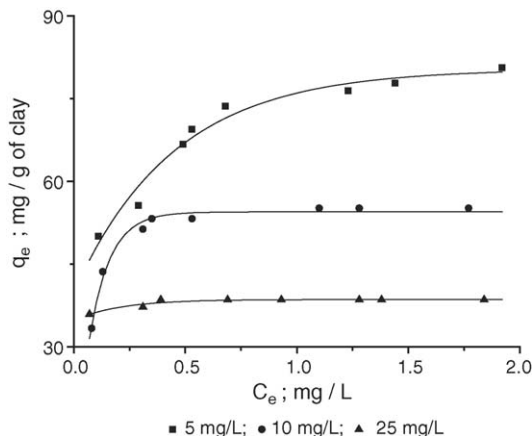


Fig. 5. Isotherms of MB retention by Na-saturated fibrous clay minerals. Clay contents: 5, 10 and 25 mg/L.

Table 1
Langmuir and Freundlich constants for isotherms relevant to MB fixation onto Na-saturated clay fibrous minerals

Clay content (mg/L)	Langmuir parameters		Freundlich parameters		Correlation coefficient (R)	
	k (L/mg)	q ₀ (mg/g)	a (mg/g)	1/n	^a L	^b F
5	8.5	85	74	0.176	0.9992	0.9691
15	26.4	57	59	0.178	0.9998	0.8884
25	489.6	39	39	0.029	0.9999	0.891

^a L, Langmuir isotherm.
^b F, Freundlich isotherm.

3.2. Equilibrium study

In Fig. 5, typical adsorption isotherms for different clay concentrations are given. These isothermal data were mathematically treated by the known Langmuir and Freundlich equations:

$$q_e = \frac{kC_e q_0}{1 + kC_e} \text{ (Langmuir equation);}$$

q_e = X_e/m and q₀ represent the equilibrium and the maximum MB uptake amounts per mass unit of adsorbent, respectively. C_e keep the same meaning and k is the Langmuir’s constant.

$$q_e = a(C_e)^{1/n} \text{ (Freundlich equation)}$$

a and n are the Freundlich’s constants.

The obtained fitting parameters for each equation are given in Table 1. By comparing the correlation coefficients, it can be deduced that the experimental isothermal curves are well described by the Langmuir equation. Moreover, it is observed that the increase of the clay concentration, C, reduces the maximum adsorption capacity, q₀, according to the equation:

$$q_0 = 37 + 48 \exp \left[-\frac{(C - 5)}{5.7} \right]$$

This is may be due to the fact that active adsorption sites are hidden because of fibers microaggregation.

Based on the fact that the Langmuir constant increases with the clay content (Table 1) and since this is proportional to the binding energy, it may be derived that the binding process becomes much energetic for concentrated clay solutions. Apparently, clay particles microaggregation occurred by means of weak attractive forces (van der Waals forces), implicating feeble energetic sites, and as a result the most active sites were forced to be placed at the free surfaces.

For more details on the mechanism of MB retention by fibrous clay minerals, MB adsorption isotherms (Fig. 6, non-linear curves) were established for acid (pH 4), neutral and alkaline (pH 9) solutions with constant ionic strength (NaCl (10⁻² mol/L)). It is found that the change of pH does not have any influence on the Langmuir isotherm-type (Fig. 6, straight lines), whereas the MB retention in the acid solution is reduced by about 20%. The latter observation is apparently due to the silanol group protonation, as previously mentioned and/or linked to the fact that in low pH values, particularly below the PZC (around 4.5 for palygorskite, the most abundant fibrous clay mineral), edge-to-face contacts “T-like texture” developed [18]. Therefore, a part of the

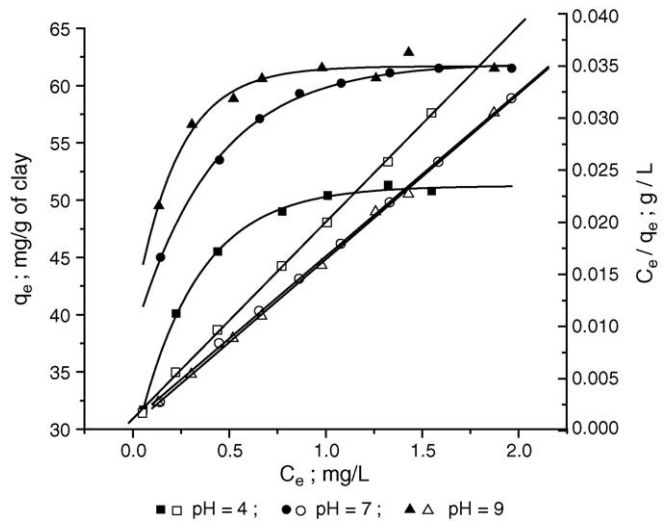


Fig. 6. Experimental and Langmuir isotherms for the MB fixation onto Na-saturated fibrous clay minerals at different pH.

activated sites is hidden. Apparently, such fibrous clay particles arrangement could not happen in alkaline solution [18]. By comparing the adsorption capacities for alkaline and acid solutions and taking into account the measured surface area, the amount of the external oxy-hydroxides is estimated to be two species per 10 nm². In other respect, by referring to Fig. 7, the change of the ionic strength does not have any appreciate impact on the MB adsorption mechanism, since the Langmuir equation holds

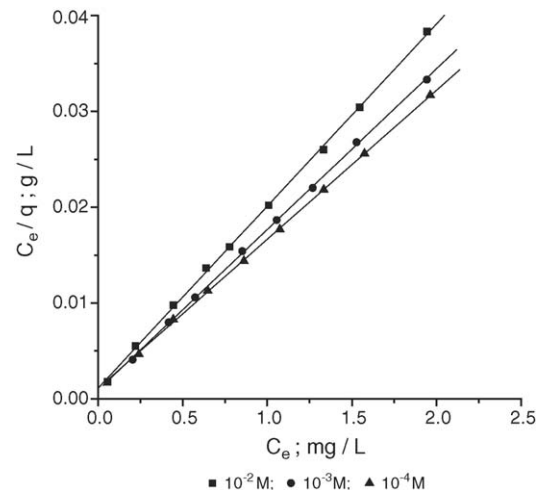


Fig. 7. Evolution of the ratio C_e/q_e for different NaCl concentrations as a function of the equilibrium MB concentration.

for all runs. However, it is observed that the adsorption capacity decreased with the increase of the ionic strength. Apparently, by increasing the ionic strength, i.e. increasing the NaCl content, the concentration of Na⁺ in the Stern layer increases and consequently the potential of the clay particles surfaces is reduced. Thereby, the electrostatic interaction between MB cations and the negative clay particles diminishes and consequently the MB diffusion towards the solid surface is restricted.

4. Conclusions

1. The MB retention from aqueous solution by fibrous minerals is a rapid process. It is controlled by solute diffusion and occurred mainly by cation-exchange phenomenon.
2. The MB adsorption isotherms established for different values of pH, ionic strength and clay content are well described by the Langmuir equation.
3. Permanent active sites are more available in diluted MB–clay suspensions. Thus, operating with reduced clay content and/or diluted MB solutions may increase the adsorption capacity beyond 85 mg/g of clay.
4. Appreciable amounts of MB can be removed by fibrous clay minerals without modifying the pH or the ionic strength of MB coloured aqueous solution.

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