Use of talc as low-cost clarifier for wastewater

Ana L. Grafia, Luciana A. Castillo and Silvia E. Barbosa

ABSTRACT

Talc is proposed as a low-cost mineral for wastewater clarification. In this sense, adsorption of methylene blue (MB) from aqueous solutions was studied comparatively by using sepiolite (qualified as very good adsorbent) and two talc samples with different particle size and purity degree. The MB adsorption was assessed by determining remnant dye in the supernatant using UV–vis spectroscopy and by detecting dye adsorbed on mineral samples through thermogravimetric analysis and infrared spectroscopy. Both isothermal curves and kinetic studies demonstrate that talc is a good dye adsorbent. Particularly, with dye concentrations similar to those of textile wastewater, talc was demonstrated to adsorb the same dye content of sepiolite at similar times. Natural talc could be employed as a low-cost alternative in wastewater treatment for the removal of cationic dyes.

Key words | adsorption, methylene blue, talc, wastewater clarification

Ana L. Grafia
Luciana A. Castillo (corresponding author)
Silvia E. Barbosa
Planta Piloto de Ingeniería Química
(UNS–CONICET),
Camino La Carrindanga Km. 7(8000) Bahía Blanca,
Argentina
E-mail: *lcastillo@plapiqui.edu.ar*

INTRODUCTION

Colored wastewater is produced as a direct result of dye production as well as a consequence of its use in textile, printing, food preparation and plastics industries. These processes consume significant water volumes, generating a considerable amount of colored effluent to be disposed (Pearce *et al.* 2003). Although dye concentration in wastewater would be low (less than 1 ppm), its presence is highly visible and undesirable. The increased restrictions on organic content of industrial effluents require finding efficient and low-cost methods to remove dyes from wastewater. Adsorption has been found to be superior to physical–chemical techniques for successful removal of different dyes from effluents. The reasons are the ease of operation, flexibility and simplicity of design, insensitivity to toxic pollutants, and relative low cost of application in the decoloration process (Rafatullah *et al.* 2010).

Several mineral particles have been employed as dye absorbents in the past. Particularly, sepiolite has been used, due to its capability to adsorb cationic dyes normally employed in tanneries as methylene blue (MB), showing greater capability than that of conventional adsorbent (El Qada *et al.* 2008). This is because of the presence of silanol groups (-SiOH) on sepiolite's external surface, which are accessible to organic species as neutral adsorption sites. In addition, its high specific surface area and large micropore volume contribute to its powerful adsorbent properties (Santos & Boaventura 2008). Depending on the world region, the use of sepiolite as adsorbent is restricted due to its relatively high price as a direct consequence of the lack of deposits. Main sepiolite mines are located in Spain, Turkey, Morocco, Greece, Tanzania and the United States. In this sense, research efforts have been focused on finding substitute adsorbents among available and cheaper minerals in order to minimize adsorption process costs. Among phyllosilicate minerals, talc could be thought as an alternative adsorbent because its structure is similar to that of sepiolite. The main difference between these minerals resides in the discontinuities and inversion of the silica sheets in the sepiolite structure, which give rise to its structural tunnels and blocks. Particularly, in Argentina there are many unexploited talc deposits due to their impurities content. As a consequence, the cost of Argentinean mineral is lower compared to high quality talc mined in Australia, Italy, France, China, Canada and the United States. Moreover, few studies were found concerning the talc use as dye adsorbent (Sener & Özyilmaz 2010; Liu *et al.* 2013).

This work aims to study comparatively MB adsorption of sepiolite, qualified as a very good dye absorbent, and two talc samples with different particle size and purity degree. Isothermal absorption curves were assessed for the three samples at the same conditions, and kinetic parameters were obtained by using two different theoretical models. Also, a comparative study of the adsorption behavior of the three samples was performed at a typical average wastewater

dye concentration, in order to analyze the feasibility of using Argentinean talc for clarification of wastewater.

EXPERIMENTAL

Materials

Commercial untreated sepiolite was provided by Tolsa Group (Spain) and talc samples by Dolomita S.A.I.C. (Argentina). Two talc samples from different origins were used: high purity (98%) Australian talc (A10) and Argentinean talc (SJ10), with up to 16 wt% impurities. Methylene blue of analytical reagent grade (Anedra) was used as dye.

Adsorption process

Weighed amounts of samples (1 g) were put in contact with MB solutions having different concentrations (55, 140, 600 and 1,200 mg/L). Then, suspensions were sonicated in a thermostated water bath at 25 °C for 3 h. The pH of the solution was adjusted to 7.5 by addition of a NaOH or HCl solution. Aliquots of solutions were taken at different times and centrifuged for 15 min at 5,000 rpm. Adsorption tests were continued until equilibrium concentration was reached. After that, the solution was centrifuged for 15 min at 5,000 rpm and solid was separated. Then, it was thoroughly washed with distilled water several times and dried in an oven at 80 °C until constant mass. From a mass-balance relationship it is possible to determine the amount of adsorbed dye per amount of dry adsorbent, defined as the adsorption capacity (q). In order to study molecule distribution between liquid and solid phase at the equilibrium, Freundlich and Langmuir models were applied. To study the mechanism of the adsorption process and potential rate controlling steps, experimental data were modeled by the pseudo-first order and the pseudo-second order models (Küncek & Sener 2010).

Characterization

Before suspension preparation, particle surface morphology and particle size distribution were examined by scanning electron microscopy (SEM) using a Jeol 35 CF microscope. SEM images were processed considering hundreds of particles by using AnalySIS2.1 (Soft-imaging Software GmbH).

Concentration of MB in supernatant solutions was determined by colorimetric method using a Shimadzu UV-160 UV–visible spectrophotometer. Absorbance measurements were made at $\lambda = 663$ nm, which corresponds to the wavelength of the maximum absorption peak of MB monomers in water. A calibration curve of absorbance against MB concentrations was plotted. Decoloration capacity (%) of MB on samples was calculated as $[C_o–C_e]/C_o \times 100$, where C_o is the initial dye concentration and C_e is the equilibrium concentration. All of the experiments were duplicated and the average value was taken.

Adsorption was corroborated assessing the presence of MB functional groups on dried samples by infrared spectroscopy with Fourier transform (FTIR) in a Nicolet 520 spectrophotometer. Dried samples were mixed with KBr powder and pressed into a thin disk. The spectrum was recorded by running 100 scans at a resolution of 4 cm^{-1} in the wavenumber range of 4,000 to 400 cm^{-1}.

Thermogravimetric analysis (TGA) was carried out in a Discovery TGA equipment from TA Instruments recording derivative thermogravimetric (DTG) curves. Samples were heated from 30 to 800 °C at 10 °C/min using an aluminum crucible in nitrogen atmosphere.

RESULTS AND DISCUSSION

Figure 1 shows SEM micrographs of samples and their respective particle size distribution curves as number-weighted histograms. Mats of interwoven sepiolite fibers are observed in Figure 1(a) where loosely packed and porous aggregates show an extensive capillary network. Figure 1(b) shows A10 talc consisting of small individual platelets which are curved due to their elasticity, corresponding to a microcrystalline morphology. These platelets are stacked on top of one another, forming round-shaped domains. Meanwhile, SJ10 particles (Figure 1(c)) appear as blocks having flatter, large and thicker cleaved platelets with abrupt and well-defined borders, all of them typical aspects of macrocrystalline talc (Ferrage *et al.* 2003). Concerning the particle size distribution, sepiolite shows a relatively broad and asymmetrical curve, having a mean value around 5.73 μm. Regarding talc samples, A10 particle size distribution is unimodal with a mean value at about 3.42 μm, and SJ10 presents a broad distribution having a mean value of 10.55 μm.

In addition, sepiolite and A10 have high purity degree; meanwhile SJ10 contains carbonates as impurities (16 wt%), as demonstrated in a previous work (Castillo *et al.* 2011). Concerning surface character, sepiolite shows a hydrophilic nature, coming from silanol groups (-SiOH). In contrast, A10 and SJ10 have amphiphilic behavior that depends on
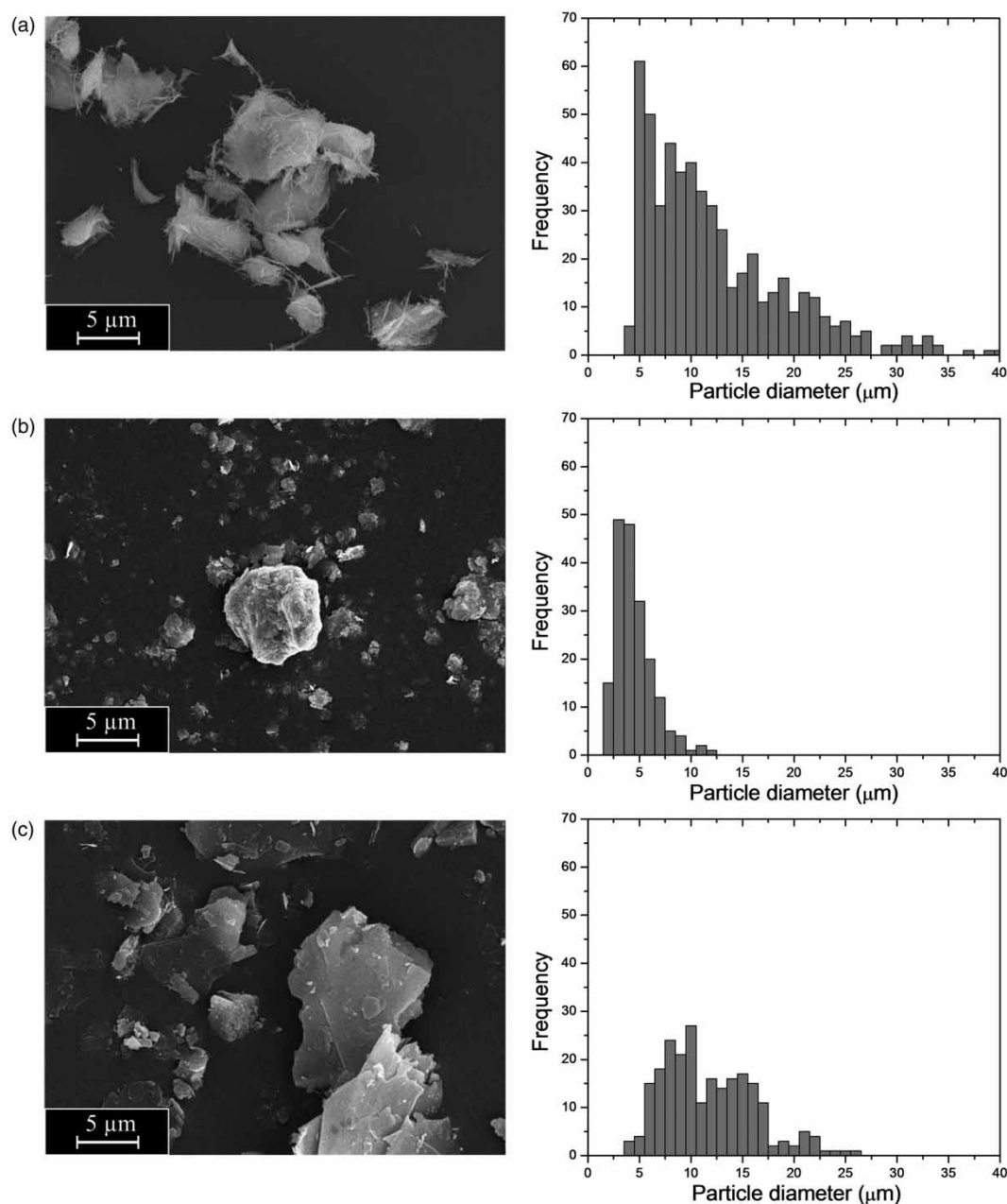
Figure 1 │ SEM micrographs (10,000 ×) and particle size distribution histograms of (a) sepiolite, (b) A10 and (c) SJ10.

the relative contribution of 'hydrophobic face' and 'hydrophilic edge' surfaces to the total area (Castillo *et al.* 2011).

Figure 2(a) presents MB breakthrough curves showing the effect of the initial dye concentration (C_o) on the adsorption process of each sample at pH 7.5 and 25 °C, using a solid/liquid ratio of 1 g/L. Initially, there was a rapid MB removal because C_o provides the driving force to overcome mass transfer resistance of dye molecules between solid and aqueous phases, and then it reached the equilibrium. The magnitude of q_e increased

with increasing C_o due to the higher number of ions competing for available adsorption sites. MB adsorption dependence on C_o is also observed in isotherms of sepiolite and talc samples (Figure 2(b)).

To study the MB adsorption isotherm on sepiolite and talc, experimental data were adjusted using Langmuir and Freundlich models. The fit quality of the isotherm to the data was analyzed based on the magnitude of the correlation coefficient (r^2). Table 1 shows isotherm parameters and r^2 values for both models. Langmuir constants include Q°,
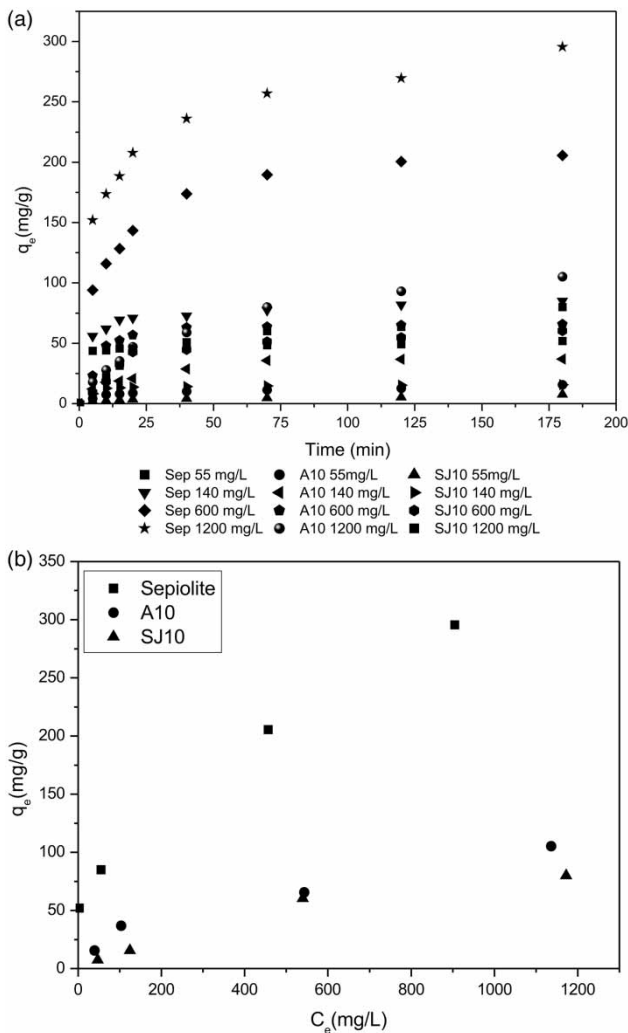
Figure 2 | (a) Effect of the initial concentration on the MB adsorption onto sepiolite and talc samples. (b) Adsorption capacity vs concentration at equilibrium (solid/liquid ratio: 1 g/L, $T = 25\,°C$).

For sepiolite, r^2 of the Langmuir isotherm is greater than that of Freundlich, indicating the existence of a MB monolayer coverage, favored by the homogeneous sepiolite surface in terms of SiOH groups. However, for A10 and SJ10, r^2 values for the Freundlich model are higher than those of Langmuir. This fact would reveal a non-specific adsorption on an energically non-uniform and heterogeneous surface, agreeing with talc structural heterogeneity (hydrophobic faces and hydrophilic edges).

Table 2 shows experimental values of adsorption capacity (q_e), rate constants of the pseudo-first order (k_1) and pseudo-second order (k_2) equations, and r^2 for MB adsorption of all samples.

To determine the controlling step of the adsorption process, experimental data were evaluated by using a pseudo-first and pseudo-second order model. Through the analysis of r^2, it can be inferred that MB adsorption kinetics on sepiolite and talc was not diffusion controlled. In this sense, MB adsorption could be explained by the pseudo-second order model, and determined q_e values were very close to that of $q_{e,exp}$. This suggests that the rate limiting step may be chemical adsorption or chemisorptions. For all samples, the rate constant of the pseudo-second order decreases with C_o due to the saturation of adsorption sites. The values of k_2 of sepiolite were higher than those for A10 and SJ10, validating the slower adsorption process of the latter samples. In addition, the experimental capacities for MB (Table 2) showed higher adsorption capacity for sepiolite than for talc samples. Concerning talc, A10 shows higher q_e values but lower k_2 than SJ10 indicating a greater amount of adsorbed MB at the equilibrium, reached at higher times than the latter sample. These differences may be attributed to talc purity degree. The presence of impurities in SJ10 talc could block the active sites for MB adsorption which lead to a lower q_e. However, higher k_2 values for SJ10 could be related to the macrocrystalline talc character (higher edge/basal surface ratio) which favors the process kinetic (Castillo *et al.* 2011). Under the studied conditions, the maximum adsorption

which is related to the maximum amount of adsorbate per unit weight of adsorbent to form a complete monolayer, and b, which accounts for the affinity of the adsorption sites. K_F and n, Freundlich constants, represent the adsorption capacity and adsorption intensity of the sorbent, respectively.

Table 1 | Langmuir and Freundlich isotherm parameters for MB adsoprtion onto sepiolite and talc samples

	Langmuir isotherm			Freundlich isotherm		
	$Q^°$ (mg/g)	b (L/mg)	r^2	K_F (mg/g)(L/mg)$^{1/n}$	n	r^2
Sepiolite	312.50	9.18×10^{-3}	0.9571	3.267	3.267	0.9464
A10	128.20	3.11×10^{-3}	0.9375	2.525	1.879	0.9654
SJ10	151.51	1.05×10^{-3}	0.9487	0.377	1.283	0.9883

Table 2 │ Adsorption capacity and kinetic parameters of pseudo-first order and pseudo-second order models for MB adsorption onto sepiolite and talc samples

		Pseudo-first order model			Pseudo-second order model		
C_o (mg/L)	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (min^{-1})	r^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg min)	r^2
Sepiolite							
55	51.96	7.75	9.21×10^{-3}	0.9384	52.08	5.53×10^{-3}	1
140	85.05	20.54	15.2×10^{-3}	0.9881	85.47	2.67×10^{-3}	1
600	205.52	109.82	26.5×10^{-3}	0.9916	208.33	0.67×10^{-3}	1
1,200	295.45	130.38	13.8×10^{-3}	0.9874	294.12	0.35×10^{-3}	0.9999
A10							
55	15.62	9.38	10.6×10^{-3}	0.9185	15.92	3.22×10^{-3}	0.9995
140	36.84	36.00	46.3×10^{-3}	0.9904	37.31	2.64×10^{-3}	0.9997
600	65.66	22.58	31.3×10^{-3}	0.8439	66.22	2.24×10^{-3}	0.9998
1,200	105.20	81.98	12.7×10^{-3}	0.9745	108.70	0.32×10^{-3}	0.9997
SJ10							
55	7.54	5.20	7.60×10^{-3}	0.9461	7.78	4.03×10^{-3}	0.998
140	15.66	4.07	18.6×10^{-3}	0.8366	15.72	3.1×10^{-3}	1
600	60.30	40.01	18.4×10^{-3}	0.849	61.35	0.97×10^{-3}	0.9996
1,200	79.93	57.03	12.2×10^{-3}	0.8334	82.64	0.41×10^{-3}	0.9987

of MB onto sepiolite was 295.45 mg/g. Regarding talc samples, the values are 105.20 and 79.93 mg/g for A10 and SJ10, respectively. When they are compared with data in literature (Küncek & Sener 2010; Liu *et al.* 2013), both talcs have relatively higher MB adsorption capacity than natural and modified talc, even compared to natural and sonicated sepiolite under the same experimental conditions.

Taking into account that there is a maximum concentration acceptable for discharge of colored industrial effluents (Wang *et al.* 2011), adsorption experiments were performed considering a mean dye initial concentration (140 mg/L). In order to study the effect of solid/liquid ratio on MB adsorption, these experiments were conducted using 1 and 17 g/L. Figure 3 shows the decoloration capacity values of sepiolite and talc for these conditions. Increasing the solid/liquid ratio (17 g/L), there is no significant difference between the decoloration capacity of sepiolite and talc. Anyway, if the solid/liquid ratio is 1 g/L, lower talc capacity could be compensated for by increasing its mass, in order to reach the same value as sepiolite. This mass excess could be afforded due to the low talc cost compared to the sepiolite cost. In this sense, talc exhibited great potential as MB adsorbent, particularly when the use of sepiolite is restricted due to its relatively high price. This claim is also valid even when talc has low purity degree,
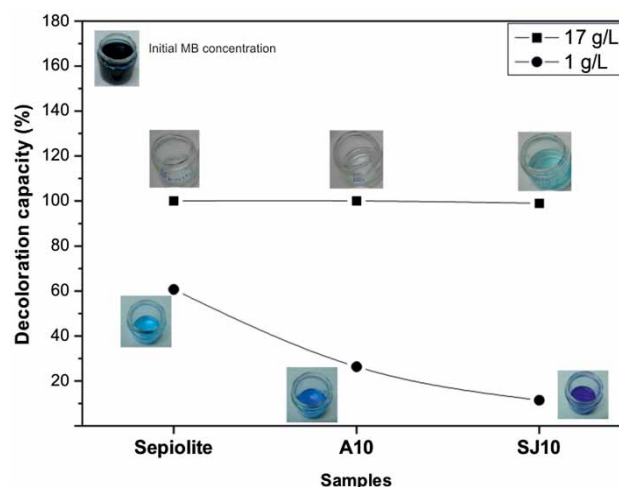
Figure 3 │ Decoloration capacity of sepiolite and talc samples including photographs of corresponding remnant solution.

as there is no significant difference in decoloration capacity between A10 and SJ10 samples.

Adsorptive removal of MB was also analyzed by using complementary techniques on solid samples after dye adsorption. The presence of adsorbed MB on samples was probed qualitatively by FTIR (Figure 4(a)). The MB spectrum shows characteristic peaks according to Imamura *et al.* (2002). Sepiolite and A10 talc show dye adsorption evidenced
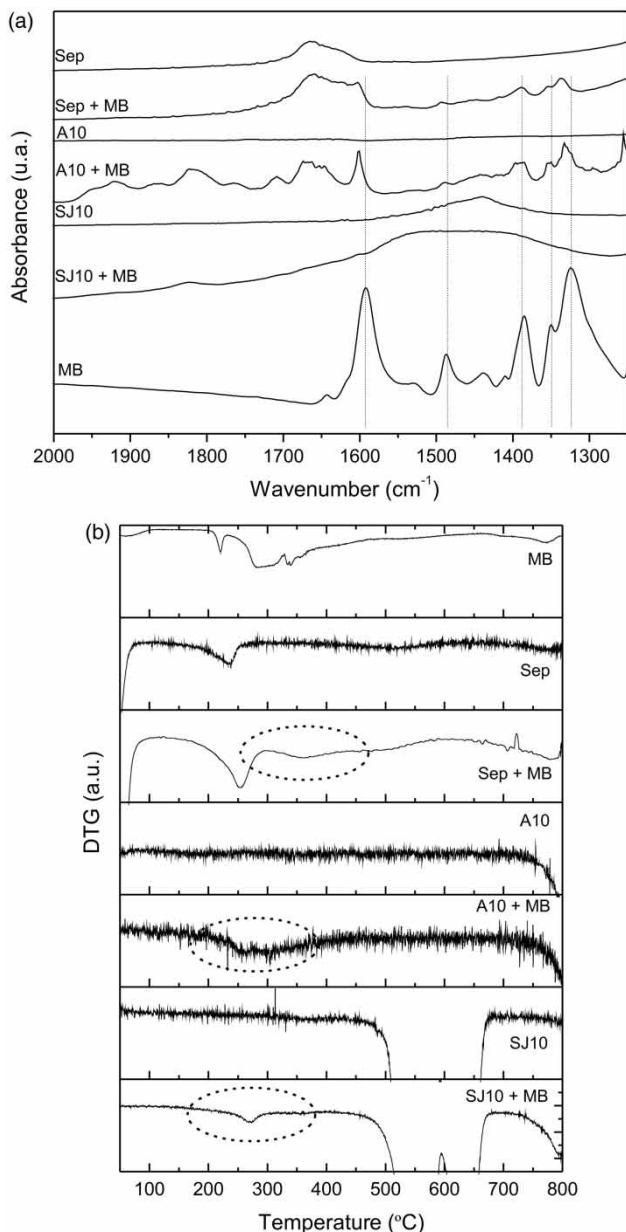
Figure 4 | (a) FTIR spectra (2,000 to 1,250 cm^{-1}) of MB and samples after dye adsorption of sepiolite and A10 talc. (b) DTG curves of MB and samples of sepiolite and talc before and after dye adsorption.

by the presence of characteristic MB bands. Despite being present, MB bands in SJ10 sample are masked by carbonate peaks. It can be observed that MB peaks' position was shifted to high wavenumbers on samples, suggesting an interaction between dye and the adsorbents' surface.

The DTG curves of MB, sepiolite and talc, before and after adsorption, are included in Figure 4(b). The evidence of MB in sepiolite and talc samples is given by the presence of the MB decomposition peak. However, it is attenuated,

indicating a very slow and gradual rate of decomposition. The onset of MB decomposition shifted to higher temperatures compared to pure dye. The MB stability up to higher temperatures in both samples, compared with pure dye, could be related to MB intercalation in sepiolite and talc, as was found by Joseph *et al.* (2009).

CONCLUSIONS

The present work aims to study comparatively MB adsorption capability of sepiolite and talc samples. According to the obtained results, talc could be employed as MB adsorbent, particularly the unexploited and abundant low-cost mineral Argentinean talc (SJ10). Australian talc (A10-high purity degree) shows higher q_e values but lower rate constant than SJ10 indicating a greater amount of adsorbed MB at the equilibrium, but at higher times than the latter sample. The presence of impurities in SJ10 talc could block the active sites for MB adsorption, which leads to a lower q_e. However, higher rate constant values for SJ10 could be related to the macrocrystalline talc character, which favors the process kinetic. Under the studied conditions, the maximum adsorption (q_m) of MB onto sepiolite was 295.45 mg/g. Regarding talc samples, q_m values are 105.20 and 79.93 mg/g for A10 and SJ10, respectively. When these values are compared with some data in literature, both talcs have relatively higher adsorption capacity for MB than natural and modified talcs, even compared to natural and sonicated sepiolite.

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