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Equilibrium and thermodynamic investigation of methylene blue adsorption on thermal- and acid-activated clay minerals

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ABSTRACT

The use of a natural Moroccan clay as an adsorbent for removal of the cationic dye methylene blue from aqueous solutions has been investigated. The starting material was activated by thermal treatment and by acid leaching with nitric acid in order to obtain samples with modified adsorption properties. The effect of the experimental conditions on the adsorption behaviour was studied by varying the treatment temperature from 373 to 1,073 K in the case of the thermally treated solids, the nitric acid concentration for the acid-activated solids and the adsorption temperature from room temperature to 368 K for both these solids. Data obtained from further batch studies were analysed using the Freundlich, Langmuir and Toth isotherm equation models. The thermodynamic parameters of the adsorption process were calculated, and the resulting Gibbs free energy indicated its spontaneity. The adsorption capacity of the clay materials makes them suitable as a low cost alternative for the removal of cationic dyes during wastewater treatment.

Keywords: Adsorption isotherm; Adsorption thermodynamics; Methylene blue; Clay acid activation; Clay thermal activation

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1. Introduction

Several industries, such as cosmetics, leather, paper, pharmaceuticals, plastics, printing and textiles, make extensive use of dyes and dyestuffs. Indeed, the textile industry is one of the main users of chemicals and water for the dyeing of fibres, cottons and wools, as a result of which it produces large amounts of coloured wastewater. The main pollutants found in textile industry wastewater, especially organic compounds, surfactants, pH modifiers and salts, cause a great danger to the environment and human health due to their potential mutagenic, carcinogenic and toxic effects [1]. The presence of residual dyes in water streams is visible and undesirable even at very low

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concentrations. As a result, there is a great need to treat dye-containing effluents prior to their discharge into receiving waters up to the limits established by currently applicable environmental regulations.

Synthetic dyes, which can be categorised as either cationic, anionic or non-ionic, are the most common pollutants in textile wastewater. In this respect, several studies have shown that around 15% of all dyes used in colouring processes can remain as pollutants in wastewater [2]. Furthermore, they have a greater tendency to persist in the environment than many other organic materials due to their aromatic structures, which provide them with an ability to resist degradation by heat, light, oxidising agents and other environmental conditions [3]. Several treatment methods, such as adsorption, biological and chemical oxidation, coagulation/flocculation, electrochemical, ion-exchange, membrane-filtration and photochemical degradation [4–6], have been applied to remove dyes from coloured wastewater. Although most of these techniques are effective for removing dyes from wastewater, they tend to be expensive, require advanced technologies and generate sludge and other products [7]. In this respect, the adsorption processes have been reported to be low cost alternatives for the removal of dyes, pigments and other chemicals from wastewater due to their simple design, easy operation and high efficiency. However, although activated carbon, for example, is a well-known adsorbent for the dye removal from wastewater [8], its high cost has restricted its use, particularly in developing countries. To overcome this problem, several researchers have applied natural, cheap, renewable and locally available adsorbents to remove dyes from aqueous solutions.

Basic Blue 9, or methylene blue (MB), is a cationic dye that is commonly used as a dyestuff. The MB can produce eye burns in humans and animals, methemoglobinaemia, cyanosis, convulsions, tachycardia, irritation to the skin, and if ingested, irritation of the gastrointestinal tract, nausea, vomiting and diarrhoea [1]. However, this dye molecule can be adsorbed on the surface of several solids and often serves as a model for removing contaminants from aqueous solutions. Previous results published in the literature concerning adsorption of this cationic dye by several adsorbents are summarised in Table 1.

In this work, the adsorption behaviour of natural Moroccan clay is evaluated by studying the adsorption of MB from aqueous solutions. The starting material was activated by thermal treatment and by acid leaching with nitric acid to obtain samples with modified adsorption properties. The effect of the experimental conditions on subsequent adsorption behaviour was studied by varying the treatment temperature from 373 to 1,073 K in the case of the thermally treated solids, the concentration of nitric acid for the acid-activated solids and the adsorption temperature from room temperature to 368 K for both these solids. The adsorption data were analysed on the basis of Freundlich, Langmuir and Toth equation isotherms and the thermodynamic parameters were also calculated. The adsorption capacity of the clay suggests that this material could be used as a low cost alternative for the removal of colour and dyes in wastewater treatment.

2. Experimental

2.1. Starting materials

The material used in the present study was a Moroccan clay mineral from the Middle Atlas region (Morocco). Chemical analysis was carried out by X-ray fluorescence spectrometry using a Philips PW 1400 spectrometer and gave the following composition (mass%): 43.73 SiO_2, 4.51 Al_2O_3, 25.39 MgO, 0.84 Fe_2O_3, 0.06 MnO, 0.04 Li_2O, 7.91 CaO, 0.69 Na_2O, 3.54 SO_3, 0.92 K_2O and 12.37 loss on ignition. This original sample is denoted by S.

The X-ray diffraction studies were carried out using a Philips PX 1820 instrument equipped with Cu Kα radiation source. The XRD pattern of the raw sample revealed the presence of contaminants such as quartz, feldspar, calcite and aragonite. Montmorillonite was identified by the peaks appearing at 2θ values of 7°, 20° and 62°.

The cation-exchange capacity (CEC) was measured according to the ammonium acetate method. Thus, the sample was first ammonium-exchanged and the ammonium ions in the supernatant deprotonated to ammonia by the addition of sodium hydroxide solution. The ammonia content was determined by distillation into a known amount of acid and back-titrated according to the Kjeldahl method. The CEC of the clay mineral obtained by this method was 0.87 meq/g.

Nitrogen adsorption experiments were performed at 77 K using a static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyser). Prior to the adsorption measurements, the samples were outgassed at 573 K for 2 h under a vacuum of less than 0.1 Pa. The BET specific surface area [17] was found to be 125 m^2/g and the micropore volume, as calculated according to the *t*-method [18], was 0.04 cm^3/g.

2.2. Thermal treatment

In order to study the effect of thermal treatment of the clay mineral on subsequent removal of the cationic

Table 1
Adsorption capacity (q_e) of methylene blue on various adsorbents

Adsorbent	q_e (mg/g)	Reference
Activated kaolin	17	[9]
Zeolite	25	[10]
Thermally activated palygorskite	78	[11]
Fibrous clay minerals	85	[12]
Montmorillonite	110	[13]
Na–ghassoulite	135	[14]
Natural bentonite	300	[15]
Activated clay minerals	500	This work
Activated carbons	916	[16]

dye, samples of the purified clay were heated in a furnace between 373 and 1,073 K for 2 h in air. After this time, the samples were allowed to cool to room temperature, then dispersed in distilled water and dried overnight at 323 K. The thermally treated samples are hereafter designated as *S–T*, where *T* indicates the treatment temperature.

2.3. Acid activation

In order to study the effect of acid treatment, 0.1 g of samples were immersed in 0.5 dm^3 of boiling HNO_3 solutions with different concentrations, without stirring, for an optimised time of 2 h. The resulting solids were washed thoroughly with distilled water and then dried at room temperature. The acid-treated samples are hereafter designated as *S–M*, where *M* indicates the concentration of the HNO_3 solution used in mol/dm^3.

2.4. Adsorption experiments

An aqueous solution of methylene blue (MB) was prepared from its chloride salt (methylene blue chloride, Merck) and diluted to the required initial concentration of between 100 and 1,200 mg/dm^3. In order to determine the equilibrium adsorption capacity of the clay mineral samples, 50 cm^3 of adsorbate solution were placed in a 100 cm^3 conical flask in a temperature-controlled bath shaker and 0.1 g of clay was added. The flasks were stoppered and then shaken for 2 h at 350 rpm. The pH was maintained at a value of 5.6 by the addition of HCl or NaOH solution. The flasks were then removed and the supernatant was centrifuged for 10 min at 9,500 rpm. The resulting MB concentration was measured using a UV–vis spectrophotometer (Standard UNICAM) at a wavelength corresponding to the maximum absorbance (663 nm). Calibration experiments were carried out in order to exclude the experimental error arising from sorption of MB on the walls of the glass vessels. The amount of MB adsorbed by the clays was calculated from the initial and final concentrations according to the following equation:

$$q_e = V \cdot (C_0 - C_e)/m \tag{1}$$

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

In order to study the effect of adsorption temperature, several additional experiments were carried out at temperatures between 290 and 368 K. Adsorption equilibrium was reached within 1 h in all the cases.

3. Theoretical approach

3.1. Adsorption isotherms

The adsorption equilibrium data of MB on modified clay minerals were fitted by applying the Freundlich, Langmuir and Toth isotherm models [19].

3.1.1. Freundlich isotherm

The Freundlich model assumes that sorption takes place on heterogeneous surfaces. This model gives a representation of the equilibrium between the amount of adsorbate in solution and that on the surface of the adsorbent,

$$q_e = k_F \cdot C_e^{1/m_F} \tag{2}$$

where k_F and m_F are empirical constants that represent the extent of adsorption and its efficacy, respectively.

3.1.2. Langmuir isotherm

The Langmuir theory assumes that a saturation point beyond which no further adsorption can occur is reached and, therefore, the saturation monolayer can be represented by the following expression:

$$q_e = \frac{q_L \cdot k_L \cdot C_e}{1 + k_L \cdot C_e} \tag{3}$$

where q_L (mg/g) and k_L (dm^3/mg) are Langmuir constants representing the monolayer adsorption capacity and the adsorption energy, respectively.

3.1.3. Toth isotherm

The Toth model is an improvement of the Freundlich and Langmuir equations. This equation accurately describes the adsorption behaviour of several adsorbates under sub-critical conditions.

$$q_e = \frac{q_T \cdot k_T \cdot C_e}{[1 + (k_T \cdot C_e)^{m_T}]^{1/m_T}} \tag{4}$$

where q_T (mg/g) and k_T (dm^3/mg) are Toth constants, representing the monolayer adsorption capacity and adsorption energy, respectively, and m_T is an empirical constant.

3.2 Thermodynamic parameters

Thermodynamic studies play an important role for fully understanding the nature of adsorption. The thermodynamics parameters related to the adsorption of MB, namely the changes in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), were therefore calculated using the following equation:

$$\Delta G = -R \times T \times \ln k \tag{5}$$

where R (8.314 J/mol·K) is the ideal gas constant, T (K) is the temperature and k (dm^3/g) is the distribution coefficient of the adsorbate (q_e/C_e), and the van't Hoff equation:

$$\ln k = \frac{\Delta S}{R} - \frac{\Delta H}{R \cdot T} \tag{6}$$

4. Results and discussion

4.1. Adsorption capacity of the clay minerals

The amount of MB adsorbed per unit mass of clay and the equilibrium concentrations in aqueous solution are presented in Fig. 1. In all cases, the adsorption efficiency and effectiveness of the clays increase with increasing initial MB concentration. The adsorptive capacity of the raw clay mineral (*S*) was found to be 350 mg/g.

In the case of the thermally modified clay minerals (see Fig. 1 (A)), the adsorption capacities were found to vary markedly depending on the treatment temperature, with treatment between 323 and 573 K improving the adsorption capacity from about 350 to 500 mg/g (see Fig. 2). Treatment at temperatures higher than 573 K resulted in a decrease in the adsorption capacity, although that for the solids heated between 673 and 873 K was still higher than that for the original sample. In contrast, heating the solids between 973 and 1,073 K resulted in a lower adsorption capacity than for the original sample. It is known that thermal activation of a clay mineral begins with the removal of water and impurities (such as organic matter and calcite, if present in the sample), with a subsequent enhancement of the clay's surface and the generation of new adsorption sites [9,20]. New porosity can also be generated by particle delamination of the clay, which may enhance the space available between the silicate layers to hold the adsorbate species at the appropriate reaction sites [21]. In the present case, these processes predominate up to 573 K, whereas at higher temperatures collapse of the clay layers, which is associated with the elimination of structural water and further dehydroxylation and therefore has a deleterious effect on the adsorption

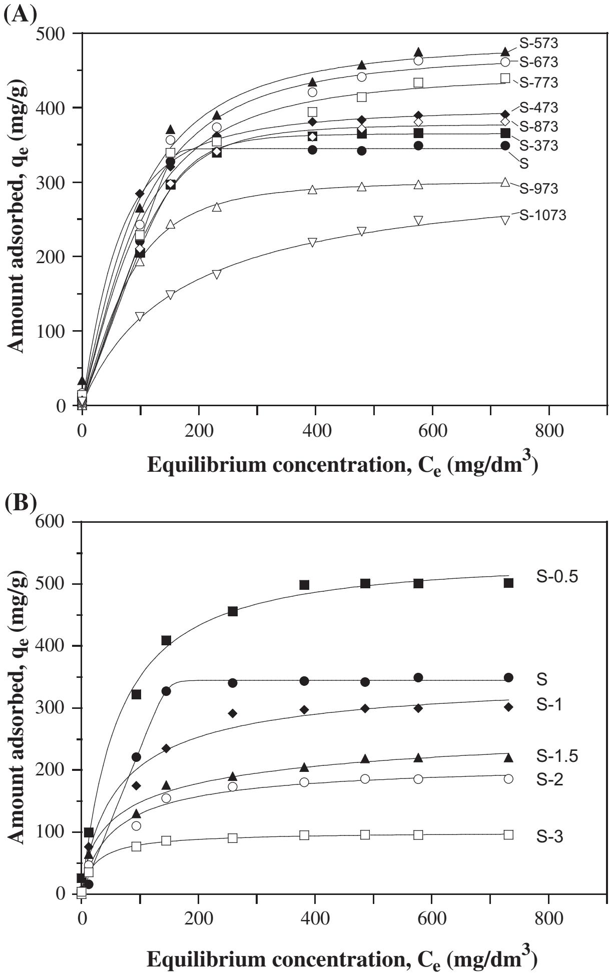

Fig. 1. Equilibrium adsorption data for methylene blue on clay minerals. (A): Thermally activated clay mineral (T = 298 K, pH = 5.6) and (B): Acid-activated clay mineral (T = 298 K, pH = 5.6).

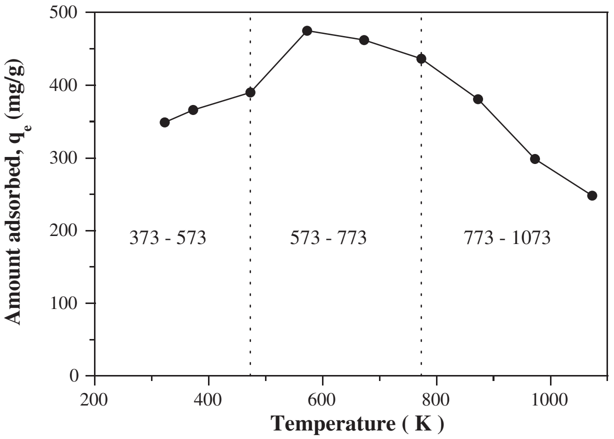

Fig. 2. The effect of thermal activation on the amount of methylene blue adsorbed.

properties, predominates. Thus, 573 K is the optimal temperature for thermal activation of the clay used in the present study, although the temperature interval between 573 and 673 K may merit a more detailed study.

The MB adsorption capacity of the acid-leached samples was found to be favoured by relatively mild treatment conditions (HNO_3, 0.5 mol/dm^3), reaching values as high as 500 mg/g (see Fig. 1(B)). Treatment with more concentrated solutions produced an important decrease in the adsorption capacity, which is even lower than that of the original sample. In the case of acid treatment of clay minerals, it is also well known that treatment under certain conditions leads to an optimal activation whereas more intense treatments result in a worsening of the adsorption properties [22]. The first step in this activation process involves exchange of the compensation cations by protons, the solubilisation of acid-soluble impurities and partial dissolution of the octahedral cations in the clay, thus giving rise to a phase similar to high-surface silica. More aggressive treatments result in passivation of the solid. The optimal point between these processes depends to a large extent on the nature of the clay mineral, the nature and concentration of the acid and the temperature. The results obtained clearly indicate that the clay used in this study is relatively sensitive to acid treatment, thus the optimal activation is reached with dilute solutions when using hot nitric acid.

In the case of the effect of adsorption temperature, the adsorption isotherms show a linear increase in adsorption capacity at low dye concentrations, thus indicating a large affinity of MB molecules for clay layers. The adsorption capacity increases slightly at low temperatures (between 290 and 313 K), thus indicating a monomolecular coverage of the dye in the interlayer spaces, probably on the external surface. It has been suggested previously [23] that, at low temperatures, a competition between dye molecules and water molecules occurs in the interlamellar spaces as a result of the strongly hydrophilic character of the clay layers. As a result, it can be proposed that the higher uptake of MB at lower temperature requires strong electrostatic interactions between the dye molecules and the active sites on the clay. The adsorption capacity increases at higher temperatures (between 313 and 353 K) because of the higher effectiveness of the interactions between the hydrophobic parts of the dye and the altered swelling properties of the clay. Indeed, the effective delamination of the clay layers that occurs at such temperatures facilitates the formation of well-defined adsorbed molecules around the exchange sites. The fact that the adsorption capacity was found to stabilise at higher temperatures (up to 368 K) can be attributed to complete delamination of the clay particles.

4.2. Modelling of MB adsorption isotherms

The adsorption equilibrium data were fitted to the Freundlich, Langmuir and Toth isotherm models. The constants for each model are used to predict the adsorption capacities and can also be incorporated into the mass transfer relationship to predict the design of contacting experiments [24]. Although taking into account that the models have different number of fitting parameters, the best fitting results were obtained using the Toth isotherm model, reason by which this isotherm was selected to be presented together with the experimental data in the figures. The parameters were estimated by non-linear regression and the values are summarised in Table 2. The estimated monolayer capacities, q_L and q_T, are in accordance with the experimental results. The product of the Toth parameters ($q_T k_T$), which is related to the interaction of the adsorbate (MB) with the surface [25], is higher for the acid-activated samples than for the thermally activated ones.

4.3. The effect of temperature on the adsorption capacity of the clay minerals

The calculated thermodynamic parameters are provided in Table 3. The plot of ln$k$ vs. 1/T allows two regions to be observed (see Fig. 3) and the linear regression and the values of ΔH and ΔS to be calculated. The results show a spontaneous and favourable adsorption process over the whole temperature range

Table 2
Freundlich, Langmuir and Toth parameters for methylene blue adsorption

	Freundlinch				Langmuir				Toth				
	k_F	m_F	R^2	χ^2	q_L (mg/g)	k_L (dm^3/mg)	R^2	χ^2	q_T (mg/g)	k_T (dm^3/mg)	m_T	R^2	χ^2
Thermal activation													
S	140	6.8	0.97	5,721	384	0.021	0.98	3,701	345	0.006	17	0.998	338
S-373	93	4.6	0.97	5,042	423	0.013	0.990	2,274	365	0.006	4	0.9994	144
S-473	153	6.7	0.995	1,121	421	0.021	0.9990	271	400	0.012	1.5	0.9993	168
S-573	101	4.1	0.98	4,699	539	0.011	0.992	2,673	491	0.008	1.6	0.993	2,412
S-673	87	3.8	0.98	4,505	531	0.010	0.993	2,259	475	0.007	1.7	0.994	1887
S-773	83	3.8	0.98	4,025	499	0.010	0.993	2,150	447	0.007	1.7	0.994	1838
S-873	87	4.3	0.98	3,897	437	0.012	0.994	1,546	377	0.006	3.0	0.998	297
S-973	91	5.4	0.992	1,150	331	0.016	0.998	312	303	0.008	2.0	0.9994	95
S-1,073	24	2.7	0.994	485	311	0.006	0.998	147	322	0.006	0.9	0.998	145
Acid activation													
S	140	6.8	0.97	5,721	384	0.021	0.98	3,701	345	0.006	17	0.998	338
S-0.5	91	3.6	0.96	16,109	558	0.016	0.995	1,710	545	0.015	1.1	0.996	1,649
S-1	55	3.7	0.96	4,943	337	0.015	0.98	1,744	358	0.020	0.8	0.98	1,662
S-1.5	42	3.8	0.98	1,247	237	0.017	0.98	921	308	0.052	0.5	0.993	466
S-2	35	3.7	0.96	1853	205	0.017	0.98	540	215	0.021	0.8	0.990	514
S-3	30	5.3	0.96	432	99	0.041	0.997	31	101	0.047	0.9	0.997	28

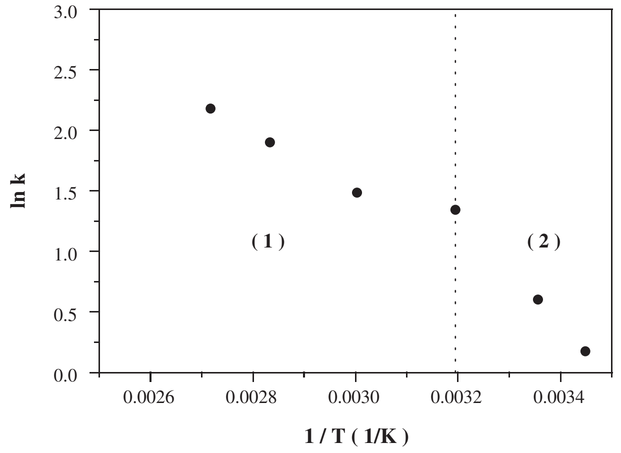

Fig. 3. Temperature intervals for the determination of the thermodynamic parameters.

Table 3
Thermodynamic parameters for methylene blue adsorption for S sample

	T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)	R^2
	290	−0.427			
(1)	298	−1.496	38.34	133.68	0.997
	313	−3.501			
	333	−4.118			
(2)	353	−5.579	20.16	72.95	0.959
	368	−6.672			

($\Delta G < 0$). The standard enthalpy change (ΔH) for the adsorption process is positive, thus indicating that the process is endothermic in nature. Furthermore, the degree of endothermicity is lowest in the second part of the curve (see Fig. 3 and Table 3), for example at above 333 K, thus indicating a more marked adsorption process. The endothermic nature of MB adsorption has been reported previously [9,26–28].

The changes in standard entropy (ΔS) are not very large. The positive adsorption entropy may depend on the degree of hydration of dye cations and/or the reorientation and restructuring of clay platelets. The positive entropy change can therefore be attributed to the increasing disorder, especially at low adsorption temperature. The entropy change decreased at temperatures above 313 K due to delamination of the clay particles, which forms an ordered system. An entropy increase has also been observed by other authors [29].

The negative values observed for the standard Gibbs free energy change (ΔG) in all the cases are indicative of the spontaneous nature of the interaction, which does not require large adsorption activation energies. As can be seen from the results presented in Table 3, the MB adsorption process becomes increasingly favourable at higher temperatures, with ΔG decreasing with increasing adsorption temperature. It can therefore be concluded that the thermodynamic processes involved in the clay–MB interaction are very uniform in nature.

5. Conclusions

The adsorption of a cationic dye (methylene blue) on a clay mineral has been studied in static mode at room temperature and atmospheric pressure. The amount of dye adsorbed at equilibrium reached 350 mg/g. Thermal and acid activation of this material improved the adsorption capacity up to 500 mg/g. The adsorption equilibrium of the MB/clay system is most suitably described by the Toth model. The adsorption follows a spontaneous physical adsorption, with Gibbs free energy values in the range −427 to −6,672 J/mol.

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