

The adsorption kinetics of the cationic dye, methylene blue, onto clay

A. Gürses^{a,*}, Ç. Doğar^c, M. Yalçın^a, M. Açıkyıldız^a, R. Bayrak^a, S. Karaca^b

^a Ataturk University, K.K. Eitim Fakultesi, Department of Chemistry, 25240 Erzurum, Turkey

^b Atatürk University, Fen-Edebiyat Fakultesi, Department of Chemistry, 25240 Erzurum, Turkey

^c Atatürk University, Erzincan Eğitim Fakultesi, Department of Science Education, 24030 Erzincan, Turkey

Received 4 July 2005; received in revised form 13 September 2005; accepted 15 September 2005

Available online 27 October 2005

Abstract

In this study, adsorption kinetics of a cationic dye, methylene blue, onto clay from aqueous solution with respect to the initial dye concentration, temperature, pH, mixing rate and sorbent dosage were investigated. In order to understand the adsorption mechanism in detail, zeta potentials and the conductivities of clay suspensions at various pH (1–11) and cation exchange capacity (CEC) were measured. Porosity and BET surface area of clay studied were determined. The results showed that the adsorption has been reached to equilibrium in 1 h. It was found that the amount adsorbed of methylene blue increases with decreasing temperature and also with increasing both sorbent dosage and increasing initial dye concentration. Adsorption capacity decreases with increasing pH, except for the natural pH (5.6) of clay suspensions. The adsorption kinetics of methylene blue has been studied in terms of pseudo-first-order, pseudo-second-order sorption and intraparticle diffusion processes thus comparing chemical sorption and diffusion sorption processes. It was found that the pseudo-second-order mechanism is predominant and the overall rate of the dye adsorption process appears to be controlled by the more than one-step.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Adsorption kinetics; Dye; Clay; Pseudo-first-order kinetics; Pseudo-second-order kinetics; Intraparticle diffusion

1. Introduction

There has been an increase for effluent being disposed to natural water bodies due to rapid industrialization. Major contaminants found in wastewater include biodegradable, volatile and recalcitrant organic compounds, toxic metals, suspended solids, plant nutrients, dyes, microbial pathogens and parasites [1,2]. Color is an effluent characteristic, which is easily detected and readily traced back to its source. Some dyes are stable to biological degradation. Consequently, there is considerable need to treat colored effluents prior to their discharge into receiving waters [3–6]. The removals of such compounds at such low levels are a difficult problem. Physicochemical techniques such as coagulation, flocculation, ozonation, reverse osmosis and adsorption on activated carbon, manganese oxide, silicagel and clays are among the methods employed [7–13]. The biological processes typically accomplish very little towards color removal [14].

Adsorption of dye at the solid/liquid interface has been extensively studied the last years. One reason for this interest is that importance of adsorption on solid surfaces in many industrial applications in order to improve efficiency and economy. Therefore, it is essential to understand the mechanism and kinetics of adsorption, because the studies of adsorption kinetics are ultimately a prerequisite for designing an adsorption column. Adsorption techniques have proven successful in removing colored organic species with activated carbon being the most widely used adsorbent due to its high capacity for the adsorption of organic materials [15–17]. However, due to its high cost and the difficulty of regeneration, a search for cheap, effective adsorbents such as bentonite clay derivatives is needed. Unlike activated carbons, clay is relatively cheap due to its accessibility and abundance [17]. In recent years, clays are important in many different fields such as agriculture, oil drilling, and the building industry. Owing to their interesting physicochemical properties (lamellar structure, high surface area, and high cation exchange capacity), clay minerals have great potential to fix pollutants such as heavy metals, dye wastewater and organic compounds [18]. Among the studied clays, expandable layered silicates (e.g., montmorillonite) as adsorbents have received considerable

* Corresponding author. Fax: +90 442 2360955.

E-mail address: ahmetgu@yahoo.com (A. Gürses).

Nomenclature

C_0	initial concentration
D	pore diffusion coefficient
h	initial adsorption rate
k_i	intraparticle diffusion rate constant
k_1	rate constant for first-order model
k_2	rate constant for second-order model
q_e	adsorbed amount at equilibrium
q_t	adsorbed amount at t time
r_0	average mean size of adsorbent
t	time
$t_{1/2}$	half-time for adsorption
m_s	sorbent dosage

recognition. An important property of the clays is that the layers are negatively charged and this negative charge is normally balanced by hydrated cations placed in the interlayer spaces. Cationic dyes, like those used in this work, can be attracted toward the anionic layers and are, therefore, quite suitable for investigating the properties of these minerals in aqueous suspensions [19]. In this respect the interaction between clay minerals and methylene blue (MB), a monovalent organic dye, has been extensively studied [20–26].

Rytwo et al. [27] have suggested the three different models for the adsorption of organic cations onto sepiolite surface:

- (i) A neutral complex may form by the electrostatically binding of a cation to a monovalent negative site on the clay block.
- (ii) A second organic cation may bind to a neutral clay–organic complex by non-coulombic interactions, forming a single positively charged complex with two organic cations and one charged site. This type of binding arises from hydrophobic interactions between large organic molecules, and may lead at high loads to charge reversal.
- (iii) A monovalently charged complex may form by the binding of one organic cation and a neutral site.

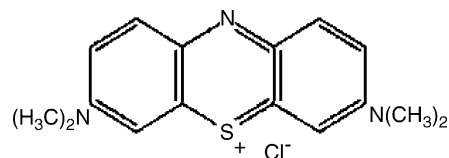
Cationic dye molecules also have very high affinity for clay surfaces and are readily adsorbed when added to clay suspensions. Therefore, these dyes were used as probes to determine several properties of the clay surfaces and the interlayer environments, like particle morphology, degree of dispersion, the extent and location of the layer charge, among others. Many of the aggregation and adsorption properties of clays can be related to the layer charge density [28]. Bujdak and Komadel [29] studied the interaction between modified clays with different layer charges and the cationic dye methylene blue in aqueous suspension. The authors concluded that the strong aggregation and redistribution of the molecules in the clays with higher layer charge was due to the proximity of the negative sites in the clay surfaces and the different coverage of the clay surfaces, suggesting that the dye is adsorbed initially only on a small fraction of the clay particles, followed by a redistribution as time passes.

The study of sorption kinetics in wastewater treatment is significant as it provides valuable insights into the reaction pathways and into the mechanism of sorption reactions. In addition, the kinetics describes the solute uptake rate that in turn controls the residence time of sorbate uptake at the solid–solution interface. Therefore, it is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate sorption treatment plants. The aim of the present work is to investigate both the adsorption mechanism and adsorption kinetics of a cationic dye, *methylene blue*, onto clay from aqueous solution with respect to the initial dye concentration, temperature, pH, mixing rate and sorbent dosage.

2. Materials and methods

2.1. Sampling

Clay samples used in this study were mineralogically mixed dominated by montmorillonite and nontronite from Erzurum region, in Turkey. The sample was air dried then sieved to give $-180+450\ \mu\text{m}$ sizes fraction using ASTM, Standard sieves. The sample was collected and stored in a jam. Chemical composition of the clay sample was determined by X-ray spectroscopy. The results are given in Table 1. The cation exchange capacity (CEC) of clay was determined by the ammonium acetate method [30]. Cation exchange capacity (CEC) is 34.4 mequiv./100 g. All chemicals used in this study were obtained from Merck. As adsorbate, a cationic dye, methylene blue (MB) was chosen. MB is a basic blue dyestuff, CI Classification Number 52015. The formula is $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}^+\text{Cl}^-$ and the structure is



2.2. BET surface area and porosity measurements

BET surface area and porosity measurements of clay sample were determined by Micrometrics FlowSorb II-2300 and Autopore II 9220 Hg Porosimeter (maximum Hg pressure 40,000 psi), respectively. The results were given in Table 2.

2.3. Effect of initial concentration

A 0.1 g sample of clay was added to each 100 mL volume of methylene blue solution. The initial concentrations of dye solu-

Table 1
Chemical composition of clay sample

Constituent	Percentage present
SiO_2	46.3
Al_2O_3	23.7
Fe_2O_3	21.6
CaO	8.4

Table 2
BET surface area and porosity of clay sample

BET surface area (m ² /g)	30.0
Average pore diameter (μm)	0.0342
Total pore surface area (m ² /g)	28.91

tion tested were 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg/L and the experiments were carried out at 20 °C in a constant temperature shaker bath.

2.4. Effect of temperature

A 0.1 g sample of clay was added to each 100 mL volume of methylene blue aqueous solution having an initial concentration 100 mg/L. The experiments were carried out at 20, 40, and 60 °C in a constant temperature shaker bath which controlled the temperature to within ±1 °C for various sorption times, in 15, 30, 60, and 120 min.

2.5. Effect of initial pH

Effect of initial pH was investigated at various pH, which are 1, 3, 5, 7, 9, and 11. In the experiments, a 0.1 g sample of clay was added to each 100 mL volume of methylene blue aqueous solution having an initial concentration 100 mg/L for a constant sorption time, 1 h.

2.6. Effect of mixing rate

A 0.1 g sample of clay was added to each 100 mL volume of methylene blue aqueous solution having an initial concentration of 100 mg/L for investigation of the effect of mixing rate at various stirring rate (90, 120, and 200 rpm). The experiments were carried out at 20 °C in a constant temperature shaker bath.

2.7. Zeta potential and conductivity measurements

Zeta potentials of solid particles in clay/water suspensions from the experiments at different initial pHs (1, 3, 5, 7, 9, and 11) were measured by using Zeta Meter 3.0+ for a constant sorption time, 60 min.

Conductivity measurements by using Karl Kolb conductometer were determined after adsorption under the same conditions as zeta potential measurements.

2.8. Adsorption experiments

In adsorption experiments, the stirring speed of 90 rpm, a 0.1 g of clay sample, methylene blue concentration of 100 mg/L was kept constant. At the end of each adsorption period, the supernatant was centrifuged for 2 min at 3750 min⁻¹. The concentration of methylene blue remaining in the supernatant after and before adsorption was determined with a 1.0 cm light path quartz cells using spectrophotometer (Shimadzu UV1201) at λ_{max} of 666 nm. The adsorbed amount of methylene blue was

calculated from the concentrations in solution before and after adsorption.

2.9. Adsorption kinetics

2.9.1. Pseudo-first-order model

In order to investigate the mechanism of adsorption, the pseudo-first-order kinetics model, the pseudo-second-order kinetics model and the intraparticle diffusion model were used to test dynamical experimental data. The pseudo-first-order model was presented by Lagergren [31]. The Lagergren's first-order reaction model is expressed as follows by Yalçın et al. [32]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

where q_e and q_t are the amounts of dye (mg/g) adsorbed on the clay at equilibrium, and at time t , respectively and k_1 is the rate constant (min⁻¹). Integrating and applying the boundary condition, $t=0$ and $q_t=0$ to $t=t$ and $q_e=q_t$ Eq. (1) takes the form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (2)$$

The rate constant, k_1 was obtained from slope of the linear plots of $\log(q_e - q_t)$ against t . For various initial dye concentrations k_1 obtained for adsorption over the first 120 min are given in Table 4 along with the corresponding correlation coefficients.

2.9.2. Pseudo-second-order model

The sorption data was also analyzed in terms of pseudo-second-order mechanism, described by [33–37]

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where k_2 is the rate constant of pseudo-second-order sorption (g/mg min). Integrating and applying boundary conditions $t=0$ and $q_t=0$ to $t=t$ and $q_e=q_t$ Eq. (3) becomes

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \quad (4)$$

which has linear form of

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (5)$$

If initial adsorption rate [38] is

$$h = k_2 q_e^2 \quad (6)$$

then Eqs. (4) and (5) become

$$q_t = \frac{t}{\frac{1}{h} + \frac{t}{q_e}} \quad (7)$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \quad (8)$$

If second-order kinetics is applicable, the plot of t/q_t against t of Eq. (8) should give a linear relationship from which the constants $q_{e,h}$ and k_2 can be determined.

The values of constants $q_{e,h}$ and k_2 for pseudo-second-order sorption have also been given in Table 4.

2.9.3. Intraparticle diffusion model

Intraparticle diffusion can be described by three consecutive steps [39]:

- (i) The transport of sorbate from bulk solution to outer surface of the sorbent by molecular diffusion, known as external (or) film diffusion.
- (ii) Internal diffusion, the transport of sorbate from the particles surface into interior sites.
- (iii) The sorption of the solute particles from the active sites into the interior surface of the pores.

The overall rate of the sorption process will be controlled by the slowest, the rate limiting step. The nature of the rate-limiting step in a batch system can be determined from the properties of the solute and sorbent. In adsorption systems where there is the possibility of intraparticle diffusion being the rate-limiting step, the intraparticle diffusion approach described by Weber and Morris [40] is used. The rate constants, for intraparticle diffusion (k_i) are determined using equation given by Weber and Morris [40]. This equation can be described as [41–43]

$$q_t = k_i t^{0.5} + c \quad (9)$$

where k_i and c are the intraparticle diffusion rate constant ($\text{mg/g min}^{1/2}$) under different initial concentration of dye and a constant, respectively. The k_i is the slope of straight-line portions of plot of q_t versus $t^{0.5}$. The values of constants, k_i and c , for intraparticle diffusion kinetics and pore diffusion coefficients have been given in Table 4. These plots have generally the double nature, i.e. initial curve portions and final linear portions. It is explained by the fact that the initial curved portions are boundary layer diffusion effects. The final linear portions are a result of intraparticle diffusion effects. An extrapolation of the linear portions of the plots back to the axis yield intercepts (c) which are proportional to the extent of boundary layer thickness [17].

3. Results and discussion

3.1. Adsorption Isotherm

The adsorption of MB onto the clay was studied for three temperatures (20, 40, and 60 °C) at different times (15, 30, 60, and 120 min), at a constant stirring speed of 90 rpm, and initial dye concentration of 100 mg/L. The adsorption isotherms for three temperatures (20, 40, and 60 °C) are given in Fig. 1. As seen from this figure, both adsorption efficiency and effectiveness of MB decreased with increasing adsorption temperature. The adsorption at the all temperatures studied usually completed when the surface of clay is covered with a monolayer of MB.

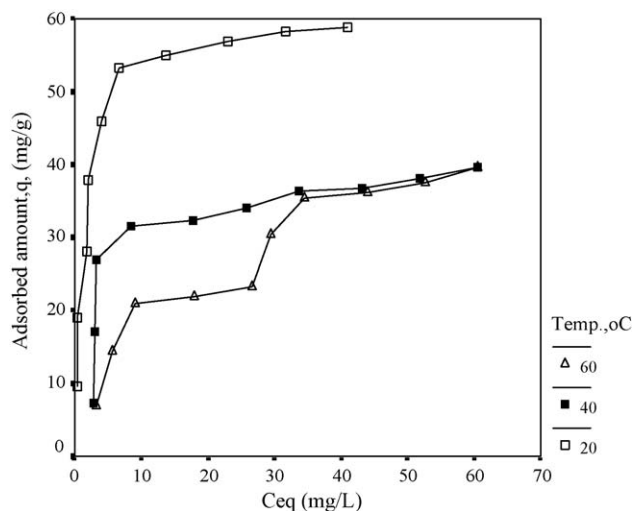


Fig. 1. The variation of the amount adsorbed vs. equilibrium concentration at various temperatures.

However, the isotherm shape for 60 °C in which there is a plateau in the range of concentration of 10–30 mg/L is different from the others. The adsorption isotherm for a cationic dye such as MB onto clay having a negatively charged surface is expected as S-shaped. However, it has been suggested [44] that an absence of S-shaped behavior at the lowest temperature may be due to the competition of dye molecules with water molecules in the inter-lamellar spaces because it is well known that the adsorption of water molecules on a solid is higher at lower temperatures [44]. Therefore, it can be said that the higher uptake of MB at lower temperature requires the intensive electrostatically interactions between the dye molecules and the active sites on the clay, comparing to dipole–dipole interactions between water molecules and the active sites on the clay. Thus, the high charged trimers (MB^+)₃ of MB stabilized at lower temperature may be responsible from the intensive interactions with the active sites on the clay through ion-pairing mechanism. The increase of the adsorption temperature could cause to the increasing of effectiveness of the interactions between the hydrophobic parts of MB and/or changing of swelling properties of clay. The isotherm for 60 °C may indicate that the monomeric form becomes dominant with increasing of the adsorption temperature and so the adsorption processes thorough ion pairing mechanism following ion exchange mechanism. In addition, the rapidly increase in the adsorption efficiency after the formation of plateau at 60 °C may be attributed to the agglomeration of MB at the relatively higher concentrations. It has been suggested that MB agglomeration and protonation were found to be sensitive to many factors, such as the dye load rate, surface properties of the clay, exchangeable cations, pH, and the age of MB-clay suspension. The greatest extent of agglomeration occurs at high dye loadings, while monomers and protonated cations predominate at low loadings [29,19].

In our previous work [45], in which the adsorption data was checked to fitting many adsorption models for the same clay and dye samples at 20, 40, and 60 °C, a high fit at 20 and 40 °C and a relatively low fit at 60 °C for Langmuir adsorp-

Table 3
Materials used as adsorbents for methylene blue

Adsorbent	Capacity (mg/g)	Reference
Wood	84	[47]
Cotton waste	24	[47]
Bentonite	150	[47]
Chrome sludge	0.51	[48]
Activated olive stones with 40 wt.% ZnCl ₂ at 873 K	16.1	[49]
Activated olive stones with 40 wt.% ZnCl ₂ at 873 K in a nitrogen atmosphere	22.1	
Activated furniture (850 °C)	200.0	[50]
Activated sewage char (800 °C)	120.0	
Activated tyres (850 °C)	130.0	
Pyrolysed furniture	80.0	
Fly ash	1.3	[51]
Zeolite	12.7	
Amorphous silica	26.5	
Banana peel	20.8	[52]
Orange peel	18.6	
Pure kaolin	15.55	[13]
NaOH-treated pure kaolin	20.49	
Calcined pure kaolin	8.88	
Activated tyre char	227.0	[53]
Clay	58.2	Present work
Raw date pits	80.3	[55]
Activated date pits (500 °C)	12.9	
Activated date pits (900 °C)	17.3	

tion model was found but not for Freundlich adsorption model. This also indicates that the adsorption of MB onto clay complete with the saturation of surface. In contrast to the adsorption isotherms for 20 and 40 °C are typically of Langmuir type, the S-shaped isotherm for 60 °C implies to lateral interactions between adsorbed species onto clay surface and/or changing agglomeration characteristics [46].

The maximum adsorption capacities of methylene blue for the adsorbent used in this study along with that of other adsorbents are presented in Table 3. Although the adsorption capacity of clay for methylene blue was low; it was much higher than that of other potential adsorbents such as cotton waste, orange and banana peel, activated olive stones and kaolin (raw and treated). According to the results obtained, clay could be employed as low-cost adsorbents and could be considered as an alternative to commercial activated carbons for the removal of color. Because of the low adsorption capacity of the activated forms of clay they were not used further.

3.2. Effect of initial dye concentration

Fig. 2 shows the effect of initial dye concentration on the adsorption rate of the dye at natural pH 5.65 and 20 °C. An increase at initial dye concentration leads to an increase in the adsorption capacity. As the initial dye concentration increases from 10 to 100 mg/L, the adsorption capacity of dye onto clay changes from 9.2 to 58.3 mg/g. This indicates that the initial dye concentration plays an important role in the adsorption capacity of dye. Dye molecules can migrate from the external surfaces to the interlamellar region, resulting in the deaggregation of the

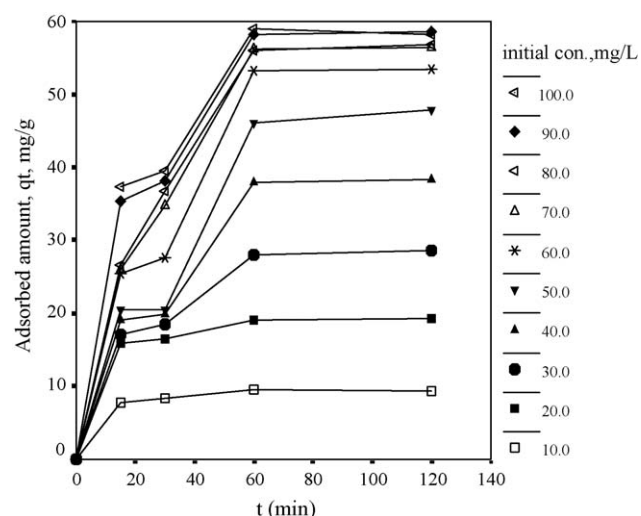


Fig. 2. The variation of the amount of adsorbed with adsorption time at various initial dye concentrations.

aggregates and restoring the monomers [28]. At high load rates of MB, agglomerates are expected to be predominant, while monomers and dimers are practically absent in MB-clay complexes [29].

The initial process, when a dye is added to the clay suspension, is the adsorption of the dye molecules onto the external surface of the particles. This increases significantly the local concentration, giving rise to the formation of aggregates of the dye.

The correlation coefficients, r_1^2 , the pseudo-first-order rate parameters, k_1 , and sorption capacity, $q_{e,1}$, for the pseudo-first-order equation for the sorption of dye, are shown in Table 4. The correlation coefficients for first-order model are rather low, namely, between 0.235 and 0.990. Therefore, it can be inferred that first-order model do not show good compliance with the experimental data.

The correlation coefficients, r_2^2 , and the pseudo-second-order rate parameters, k_2 , are shown for the pseudo-second-order equation for the sorption of dye and compared with r_1^2 , r_1^1 and k_1 , k_i values for the pseudo-first-order reaction mechanism and intra-particle model in Table 4. The data shows a good compliance with the pseudo-second-order equation and the regression coefficients for the linear plots were higher than 0.869. It is clear that the kinetics of dye sorption onto clay follows the pseudo-second-order rate expression. The equilibrium sorption capacity, $q_{e,2}$, increased from 9.63 to 65.5 mg/g when the initial concentration of dye increased from 10 to 100 mg/L (Table 4), indicating that the dye removal is dependent on initial concentration. While the initial concentration varies from 10 to 50 mg/L, the rate constant, k_2 , decrease from 33.2×10^{-3} to 0.33×10^{-3} . In initial concentration range 60–100 mg/L, rate constant increases from 0.56×10^{-3} to 1.1×10^{-3} . The values of the initial sorption rates, h , were shown in Table 4. While the initial concentration varies from 10 to 50 mg/L, the initial sorption rate, h , decrease from 3.08 to 1.50. While the C_0 varies from 60 to 100 mg/L, the initial sorption rate, h , increase from 2.27 to 4.98.

Table 4
Parameters for effect of initial concentration for methylene blue

Initial dye concentration, C_0 (mg/L)	Pseudo-first-order model		Pseudo-second-order model		Intraparticle diffusion					
	$q_{e,1}$, pre.	k_1 ($\times 10^{-3}$ min $^{-1}$)	$q_{e,2}$, pre. (mg/g)	k_2 ($\times 10^{-3}$ g/mg min)	h (mg/g min)	Rate constant, k_i (mg/g min $^{1/2}$)	r_1^2	Intercepts, c (from Eq. (9))	$t_{1/2}$ (from Eq. (9))	D ($\times 10^{-6}$ cm 2 s $^{-1}$)
10	28.8	0.703	9.63	33.2	3.08	0.767	0.997	5.76	3.0	3.15
20	21.4	0.690	20.0	11.0	4.39	1.198	0.943	12.4	4.6	2.05
30	19.1	0.235	33.3	1.80	2.00	1.215	0.913	4.35	18.5	0.51
40	20.4	0.640	50.0	0.67	1.68	1.138	0.854	-3.24	37.1	0.25
50	19.5	0.870	67.1	0.33	1.50	0.869	0.830	-10.3	60.0	0.16
60	13.5	0.840	64.0	0.56	2.27	1.962	0.880	-7.18	30.2	0.31
70	9.62	0.810	69.5	0.60	2.88	2.519	0.979	-6.05	23.9	0.39
80	7.98	0.713	60.0	0.65	3.10	3.117	0.994	-3.62	19.2	0.49
90	3.32	0.990	64.8	1.0	4.37	4.677	0.908	8.99	10.7	0.88
100	1.73	0.915	65.5	1.1	4.98	5.916	0.891	12.4	8.6	1.1

The corresponding linear plots of the values of $q_{e,2}$, k_2 and h against C_0 were regressed to obtain expressions for these values in terms of the initial dye concentration with high correlation coefficients (Table 4). Therefore, it is further considered that $q_{e,2}$, k_2 and h can be expressed as a function of C_0 for dye as follows:

$$k = \frac{C_0}{5 \times 10^2 C_0 - 5 \times 10^3}, \quad r^2 = 0.925 \quad (10)$$

$$q_e = 1.62C_0 - 9.6 \times 10^{-3}C_0^2, \quad r^2 = 0.991 \quad (11)$$

$$h = 0.21C_0 - 5.1 \times 10^{-3}C_0 + 5 \times 10^{-5}C_0^2, \quad r^2 = 0.910 \quad (12)$$

Substituting the values of $q_{e,2}$ and h from Table 4 into Eq. (7), the relationship of q_t , C_0 and t can be represented as follows:

$$q_t = \frac{t}{\frac{1}{0.21C_0 - 5.1 \times 10^{-3}C_0 + 5 \times 10^{-5}C_0^2} + \frac{t}{1.62C_0 - 9.6 \times 10^{-3}C_0^2}} \quad (13)$$

Eq. (13) can be used to derive the amount of dye sorbed onto clay at any given initial dye concentration and contact time, at the pH of 5.65 and within amount of sorbent, 0.10 g.

As seen from Table 4, the equilibrium sorption capacities and correlation coefficients for second-order model are much more reasonable when compared with experimental results than that of the first-order model. Since most of the first-order $q_{e,1}$ values deviate significantly from the experimental values, it suggests that the sorption of dye onto clay follows the pseudo-second-order model. Further, there was very minor deviation between expected and observed $q_{e,2}$ (amount of dye adsorbed at equilibrium, mg/g) values. It can be said that more than one-step may be involved in sorption process. In addition, for first-order model the intercept of the straight line plots of $\log(q_{e,1} - q_t)$ against t should be equal to $\log q_e$. If this not the case, it suggests that the sorption would not be a first-order reaction even if the linearized plots have higher correlation coefficients than other two mechanisms. From Table 4, this suggests that dye adsorption does not follow a first-order kinetic mechanism. Because second-order model assumes the rate-limiting step may be the sorption in agreement with chemical sorption being the rate-controlling step, which may involve valence forces through sharing or exchange of electrons between dye and adsorbent. Bujdak and Komadel [29] reports that the cations are adsorbed via ion exchange, frequently accompanied by agglomeration, where micelles consisting of three or more cations at the clay surface orient via π - π interaction on both sides of the molecular plane with two neighboring cations. Also, this situation shows in aqueous medium, the role of the exchangeable alkali and other metal cations on the surface and in the interlayer region of the clay.

3.2.1. Intraparticle diffusion model

The sorption kinetic data were further processed to determine whether intraparticle diffusion is rate limiting and to find rate parameter for intraparticle diffusion (k_i). The correlation coefficients of the intraparticle diffusion model are given in Table 4

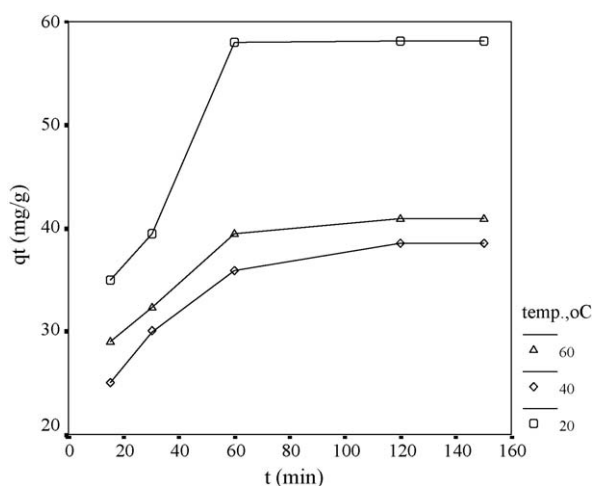


Fig. 3. Effect of temperature on the adsorption of methylene blue onto clay.

for the different initial concentrations and although all high (>0.830), they are significantly lower than that of the second-order kinetic model. This suggests that the pseudo-second-order adsorption mechanism is predominant and that the overall rate of the dye adsorption process appears to be controlled by the more than one-step [34,35].

3.3. Effect of temperature

Fig. 3 shows the effect of temperature on adsorption of dye onto clay at pH 5.65 at dye concentration 100 mg/L. The increase in temperature (from 20 to 40 °C) leads to a decrease in dye uptake, but when the temperature varies from 40 to 60 °C, the uptake increases. After the equilibrium, the decrease in dye uptake in the temperature interval, 20–40 °C, indicates the exothermic nature of adsorption (see Table 6 for isosteric adsorption enthalpy value) [54]. However, a slight increase in dye uptake in temperature interval, 40–60 °C, shows endothermic adsorption process.

Table 5 lists the results of rate constant studies for different temperatures calculated by the three models. From Table 5 depicts that the pseudo-second-order adsorption model for the adsorption of dye onto clay and the correlation coefficients (r^2) indicate that the dye sorption onto clay does not follow pseudo-first-order kinetic model for 20 °C. The correlation coefficients (r^2) for the pseudo-second-order adsorption model (see Table 5) have the highest values (>0.989), suggesting the dye adsorption process is predominant by the pseudo-second-order adsorption mechanism. For the pseudo-second-order model, the rate constant increases significantly with increasing of temperature from 20 to 60 °C. The initial adsorption rate firstly decreases from 4.52 to 3.88 mg/g min with increasing temperature and then increases from 3.88 to 5.10 mg/g min. In Table 5, the rate constant at 20, 40 and 60 °C are 0.00103, 0.00202 and 0.00263 g/mg min, respectively. While temperature increases from 20 to 40 °C, the increase in rate constant is nearly twice time of the increase in temperature interval 40–60 °C. The change of the adsorption capacity is not influenced with increasing temperature. The change in adsorption capacity with increasing temperature can

Table 5
Parameters for effect of temperature for methylene blue

Temperature (°C)	Pseudo-first-order model		Pseudo-second-order model			Intraparticle diffusion				
	$q_{e,1,pre}$	r_1^2	k_1 (min^{-1})	$q_{e,2,pre}$ (mg/g)	k_2 (g/mg min)	h (mg/g min)	Rate constant, k_i ($\text{mg/g min}^{1/2}$)	r_1^2	Intercepts, c (from Eq. (9))	$t_{1/2}$ (from Eq. (10))
20	27.5	0.793	0.0469	66.23	0.00103	4.52	6.10	0.944	9.50	9.7
40	38.9	0.990	0.0555	44.02	0.00202	3.88	2.80	0.997	14.3	4.6
60	33.9	0.993	0.0474	44.05	0.00263	5.10	2.74	0.987	18.0	3.8
20							0.05	0.922	57.6	
40							0.62	0.922	31.2	
60							0.34	0.922	37.0	

Table 6
Activation energy and isosteric adsorption enthalpy values for adsorption of dye onto clay

Temperature interval (°C)	Activation energy, E_a (kJ/mol)	$(\Delta H_{ads})_y$ (kJ/mol)
20–40	25.6	–7.99
40–60	11.4	

be attributed to the exothermic nature of process. The adsorption capacity decreases with increasing temperature indicates that the adsorption process occurs through physical interactions.

As seen from Table 5, the equilibrium sorption capacities and correlation coefficients for second-order model are much more reasonable when compared with experimental results than that of the first-order system. Since the first-order $q_{e,1}$ values deviate significantly from the experimental values, it suggests that the sorption of dye onto clay follows the pseudo-second-order model. It can be said that more than one-step may be involved in sorption process. In addition, this suggests that the adsorption of dye does not follow a first-order kinetic mechanism.

Changing temperature from 20 to 40 °C, an increase in the amount adsorbed suggests that sorption process has an endothermic character. While temperature varies from 40 to 60 °C, the uptake decreases indicating that an exothermic process controls the adsorption of dye. E_a values for the two distinct temperature interval are given in Table 6. Although, the values of activation energy implies to a chemical sorption process, it can be said that the predominant adsorption mechanism is physical, considering the value for the isosteric sorption enthalpy (–7.99 kJ/mol).

3.3.1. Intraparticle diffusion model

For the sorption of dye, the correlation coefficients of the intraparticle diffusion model are given in Table 5 for the different temperatures. Although all high (>0.922), they are lower than that of for the second-order kinetic model. These suggest that the pseudo-second-order adsorption mechanism is predominant and that the overall rate of the dye adsorption process appears to be controlled by the chemical reaction [34,35]. However, the correlation coefficients for both intraparticle diffusion and second-order kinetic models above 40 °C are high and close to each other. At especially 60 °C the effectiveness of the adsorption is extremely low, although the efficiency of adsorption at higher concentrations is higher. Therefore, it can also be said that the overall rate of the dye adsorption process is controlled by both diffusion of dye cations to interlayer spaces and the extent of interactions between dye cations and active sites on the clay.

3.4. Effect of sorbent dosage

The effect of sorbent dosage on the adsorption rate of the dye at natural pH 5.65 and 20 °C was investigated. The results were shown in Fig. 4. An increase in sorbent dosage leads to an increase in the adsorption capacity. While sorbent dosage increases from 0.10 to 0.30 g at adsorption time of 120 min, the adsorption capacity of dye onto clay changes from 57.1 to 66.1 mg/g. Increasing the adsorbent dosage at a fixed MB con-

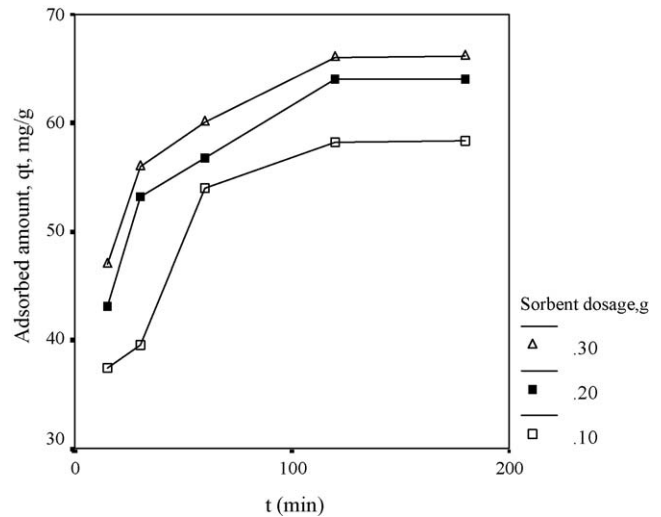


Fig. 4. Effect of sorbent dosage on the adsorption of methylene blue onto clay.

centration provided more available adsorption sites for MB and thus increased the extent of MB removal [55]. The fit to the various kinetics models of data and the parameters calculated by model are given in Table 7.

The correlation coefficients, r_1^2 , the first-order rate parameters, k_1 , and sorption capacity, $q_{e,1}$ for the pseudo-first-order equation for the sorption of dye are shown in Table 7. The correlation coefficients for first-order model are low, namely, between 0.939 and 0.977. Therefore, it can be inferred that first-order model do not show good compliance with experimental data. The correlation coefficients, r^2 , the pseudo-second-order rate constant, k , and equilibrium sorption capacity, q_e , were calculated and presented in Table 7. It is evident that the kinetic of dye sorption on the clay follows a pseudo-second-order rate expression, because correlation coefficient for second-order model is higher than first-order model. With increasing sorbent dosage, both initial rate, h , and rate constant, k , increases. This imply that the number of active sites increase as parallel to increasing sorbent dosage. For the sorption of dye, the correlation coefficients of the intraparticle diffusion model are given in Table 7 for the different sorbent amount and although all high (>0.906), they are lower than those of for the second-order kinetic model.

The corresponding linear plots of the values of $q_{e,2}$, k_2 and h against clay dose, m_s , were regressed to obtain expressions for these values in terms of m_s with high correlation coefficients. Therefore, it is further considered that $q_{e,2}$, k_2 and h can be expressed as a function of m_s for dye as follows:

$$k = 2.57 \times 10^{-3} + 6.55 \times 10^{-3} \log m_s, \quad r^2 = 0.999 \quad (14)$$

$$h = 13.2 + 3.8 \log m_s, \quad r^2 = 0.999 \quad (15)$$

$$q_e = 75.4(m_s)^{0.061}, \quad r^2 = 0.995 \quad (16)$$

$$q_t = \frac{t}{\frac{1}{13.2+3.8 \log m_s} + \frac{t}{75.4(m_s)^{0.061}}} \quad (17)$$

Table 7
Parameters for effect of sorbent dosage for methylene blue

Sorbent dosage (g)	Pseudo-first-order model		Pseudo-second-order model			Intraparticle diffusion				
	$q_{e,1,pre}$	k_1 (min^{-1})	$q_{e,2,pre}$ (mg/g)	k_2 (g/mg min)	h (mg/g min)	r_1^2	r_2^2	Rate constant, k_i ($\text{mg/g min}^{1/2}$)	Intercepts, c (from Eq (9))	$t_{1/2}$ (from Eq. (10))
0.10	$10^{4.27}$	0.977	65.4	0.00106	4.52	0.994	0.994	3.21	24.74	11.6
0.20	$10^{4.13}$	0.939	68.5	0.00151	7.09	0.998	0.998	2.72	35.02	8.50
0.30	$10^{3.80}$	0.960	69.9	0.00178	8.70	0.999	0.999	2.49	39.75	7.26

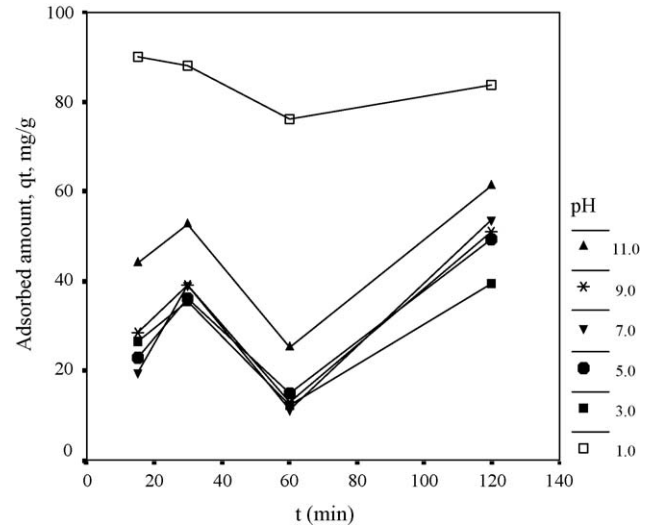


Fig. 5. Effect of initial suspension pH on the adsorption of methylene blue onto clay.

3.5. Effect of initial pH

The variation of adsorption of MB onto clay with adsorption time was investigated as a function of initial suspension pH. The data graphed in Fig. 5 did not reveal a good compliance with any kinetics models studied for the other parameters. The variations of both the zeta potentials of particles and the amount adsorbed of the MB onto clay with initial pH were investigated in the range of pH 1–11 and the results are given in Fig. 6. The variation of both the zeta potentials of particles and electrical conductivity values with initial pH were also presented in Fig. 7. The adsorption of dye from aqueous solution onto surface of clay is highly dependent on pH of the solution that affects the both surface properties and topography of the sorbent and dye structure. The methylene blue adsorption showed a minimum at pH 3 and 7 while the maximum adsorption values of methylene blue were obtained at pH 1 and 5.6 (in Fig. 6). Although the high uptake of MB at natural pH (5.6) is difficult to explain, it can be said that the adsorptive characteristics of the clay below and above the natural pH was changed, depending on the changing of

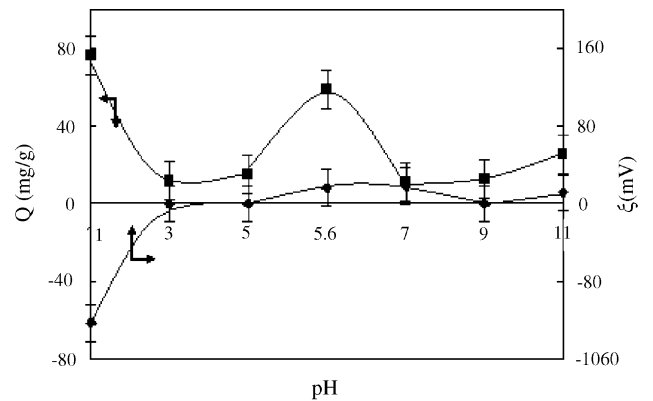


Fig. 6. The variation of both the amount adsorbed and zeta potential with suspension pH. Adsorption temperature: 293 K, adsorption time: 60 min, stirring speed: 90 rpm and C_{int} :100 mg/L.

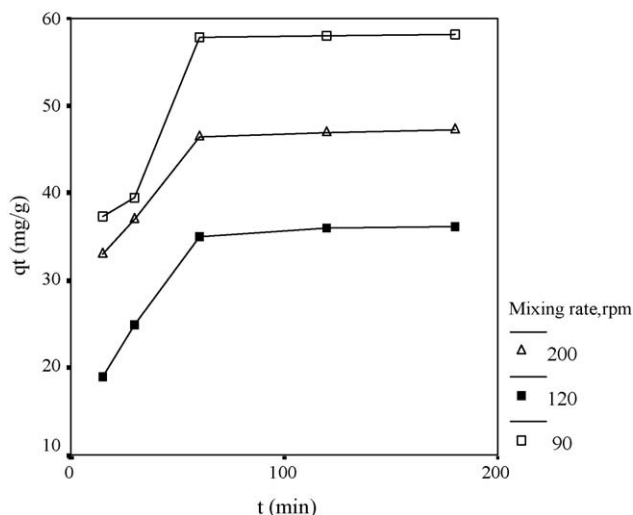


Fig. 8. Effect of mixing rate on the adsorption of methylene blue onto clay.

increases significantly with increasing of mixing rate from 90 to 200 rpm. The initial adsorption rate firstly decrease from 4.93 to 2.79 mg/g min with increasing mixing rate and then increase from 2.79 to 6.85 mg/g min. In Table 8, the rate constants at 90, 120, and 200 rpm are 0.00115, 0.00177, and 0.00280 g/mg min, respectively. While mixing rate increases from 120 to 200 rpm, the increase in rate constant is nearly twice time of the increase in mixing rate interval 90–120 rpm. The correlation coefficients of the intraparticle diffusion model are given in Table 8 for the different mixing rate. The data are lower than those of for the pseudo-second-order kinetic model.

As seen from Table 8, the equilibrium sorption capacities and correlation coefficients for second-order model are much more reasonable when compared with experimental results than that of the first-order system and intraparticle diffusion kinetics. Since the first-order $q_{e,1}$ values deviate significantly from the experimental values, it suggests that the sorption of dye onto clay follows the pseudo-second-order model. It can be said that more than one-step may be involved in sorption process. This suggests that the adsorption of dye does not follow a first-order kinetic mechanism and intraparticle diffusion kinetic model.

4. Conclusions

Clay mineral crystals carry a charge arising from isomorphous substitutions of certain atoms in their structure for other atoms of a different valence. In the tetrahedral sheet, Si(IV) may be replaced by trivalent cations, or divalent cations may replace Al(III) in the octahedral sheet. When this is the case, charge deficiency results and negative potential at the surface of the clay is created. The negative potential is compensated by the adsorption of cations on the surface. The total number of cations adsorbed on the clay is called the cation exchange capacity CEC [18].

In this study, it was found that the sorption tends to attain the equilibrium in nearly 60 min. The maximum removal capacity for initial dye concentration, 100 mg/L, was 58.2 mg/g. Also, a comparison of the kinetic models on the overall adsorption rate showed that dye/clay system was best described by the pseudo-

second-order rate model and sorption can not be described with first-order model or intraparticle model. $q_{e,2}$, k_2 and h can be expressed as a function of m_s and C_0 for dye. MB was adsorbed by clay in greater amounts than their CEC values. The sorption maxima of organic cations exceed the CEC of clay minerals, showing that besides the contribution of CEC, sorption takes place on neutral sites and neutral complexes that are formed through sorption of an organic cation on a negative site. Margulies et al. [20] showed that the clay particles moved to the negative electrode if adsorption of the organic cations was in excess of the CEC. Some researchers have discussed the sorption of organic cations on a negatively charged site that is already neutralized. Organic cation sorption on neutral sites and neutral complexes results in a charge reversal of the surfaces, which in turn alters the sorption characteristics, and colloid behavior of the clays [20,22].

References

- [1] G. Bitton, Wastewater Microbiology, John Wiley & Sons, Inc., USA, 1994, pp. 63–65.
- [2] M. Sidat, H.C. Kasan, F. Bux, Laboratory-scale investigation of biological phosphate removal from municipal wastewater, Water SA 25 (1999) 459–462.
- [3] V.J.P. Poots, G. McKay, J.J. Healy, Removal of acid dye from effluent using natural adsorbents. 1. Peat, Water Res. 10 (1976) 1061–1066.
- [4] V.J.P. Poots, G. McKay, J.J. Healy, Removal of acid dye from effluent using natural adsorbents. 2. Wood, Water Res. 10 (1976) 1067–1070.
- [5] G. McKay, M.S. Otterburn, A.J. Aga, Fullers earth and fired clay as adsorbents for dyestuffs—equilibrium and rate studies, Water Air Soil Pollut. 24 (1985) 307–322.
- [6] M. Doğan, M. Alkan, Y. Onganer, Adsorption of methylene blue from aqueous solution onto perlite, Water Air Soil Pollut. 120 (2000) 229–248.
- [7] A. Gürses, M. Yalçın, Ç. Doğar, Investigation on settling velocities of aluminium hydroxide-dye flocs, Fresenius Environ. Bull. 12 (2003) 16–23.
- [8] M. Pollock, Neutralizing dyehouse wastes with flue gases and decolorizing with fly ash, Am. Dyestuff Rep. 62 (1973) 21–23.
- [9] I. Arvanitoyannis, I. Eleftheriadis, E. Kavrentis, Treatment of dye-containing effluents with different bentonites, Chemosphere 16 (1987) 2523–2529.
- [10] I. Arvanitoyannis, I. Eleftheriadis, E. Tsatsaroni, Influence of pH on adsorption of dye-containing effluents with different bentonites, Chemosphere 18 (1989) 1707–1711.
- [11] N. Nyholm, B.N. Jacobsen, B.M. Pederson, O. Poulsen, A. Damborg, B. Schultz, Removal of organic micropollutants at ppb levels in laboratory activated-sludge reactors under various operating-conditions—biodegradation, Water Res. 26 (1992) 339–353.
- [12] P. Mavros, A.C. Daniilidou, N.K. Lazaridis, L. Stergiou, Color removal from aqueous-solutions. 1. Flotation, Environ. Technol. 15 (1994) 601–616.
- [13] D. Ghosh, K.G. Bhattacharyya, Adsorption of methylene blue on kaolinite, Appl. Clay Sci. 20 (2002) 295–300.
- [14] A. Gürses, M. Yalçın, Ç. Doğar, Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables, Waste Manage. 22 (2002) 491–499.
- [15] B. Chen, C.W. Hui, G. McKay, Pore-surface diffusion modeling for dyes from effluent on pith, Langmuir 17 (2001) 740–748.
- [16] R.S. Juang, F.C. Wu, R.L. Tseng, The ability of activated clay for the adsorption of dyes from aqueous solutions, Environ. Technol. 18 (1997) 525–531.
- [17] L. Markovska, V. Meshko, V. Noveski, M. Marinovski, Solid diffusion control of the adsorption of basic dyes onto granular activated carbon

- and natural zeolite in fixed bed columns, *J. Serbian Chem. Soc.* 66 (2001) 463–475.
- [18] C. Bilgiç, Investigation of the factors affecting organic cation adsorption on some silicate minerals, *J. Colloid Interf. Sci.* 281 (2005) 33–38.
- [19] A.P.P. Cione, M.G. Neumann, F. Gessner, Time-dependent spectrophotometric study of the interaction of basic dyes with clays. III. Mixed dye aggregates on SWy-1 and laponite, *J. Colloid Interf. Sci.* 198 (1998) 106–112.
- [20] L. Margulies, H. Rozen, S. Nir, Model for competitive adsorption of organic cations on clays, *Clays Clay Miner.* 36 (1988) 270–276.
- [21] G. Rytwo, C. Serban, S. Nir, L. Margulies, Use of methylene blue and crystal violet for determination of exchangeable cations in montmorillonite, *Clays Clay Miner.* 39 (1991) 551–555.
- [22] G. Rytwo, S. Nir, L. Margulies, Interactions of monovalent organic cations with montmorillonite-adsorption studies and model-calculations, *Soil Sci. Soc. Am. J.* 59 (1995) 554–564.
- [23] G. Rytwo, S. Nir, L. Margulies, B. Casal, J. Merino, E. Ruiz-Hitzky, J.M. Serratos, Adsorption of monovalent organic cations on sepiolite: experimental results and model calculations, *Clays Clay Miner.* 46 (1998) 340–348.
- [24] R.A. Schoonheydt, L. Heughebaert, Clay adsorbed dyes: methylene blue on laponite, *Clay Miner.* 27 (1992) 91–100.
- [25] C. Breen, B. Rock, The competitive adsorption of methylene blue on to montmorillonite from binary solution with thioflavin T, proflavine and acridine yellow. Steady-state and dynamic studies, *Clay Miner.* 29 (2) (1994) 179–189.
- [26] Y.G. Mishael, G. Rytwo, S. Nir, M. Crespin, F. Annabi-Bergaya, H. Van Damme, Interactions of monovalent organic cations with pillared clays, *J. Colloid Interf. Sci.* 209 (1999) 123–129.
- [27] G. Rytwo, D. Tropp, C. Serban, Adsorption of diquat, paraquat and methyl green on sepiolite: experimental results and model calculations, *Appl. Clay Sci.* 20 (2002) 273–282.
- [28] M.G. Neumann, F. Gessner, C.C. Schmitt, R. Sartori, Influence of the layer charge and clay particle size on the interactions between the cationic dye methylene blue and clays in an aqueous suspension, *J. Colloid Interf. Sci.* 255 (2002) 254–259.
- [29] J. Bujdak, P. Komadel, Interaction of methylene blue with reduced charge montmorillonite, *J. Phys. Chem. B* 101 (1997) 9065–9068.
- [30] J.D. Rhoades, Cation exchange capacity, in: *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties*, 2nd ed., American Society of Agronomy/Soil Science Society of America, Madison, WI, USA, 1982, pp. 149–157.
- [31] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens, Handlingar* 24 (4) (1898) 1–39.
- [32] M. Yalçın, A. Gürses, Ç. Doğan, M. Sözbilir, The adsorption kinetics of cethyltrimethylammonium bromide (CTAB) onto powdered active carbon, *Adsorption* 10 (2004) 339–348.
- [33] R.L. Tseng, F.C. Wu, R.S. Juang, Liquid-phase adsorption of dyes and phenols using pinewood-based activated carbons, *Carbon* 41 (2003) 487–495.
- [34] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Eng. J.* 70 (1998) 115–124.
- [35] Y.S. Ho, G. McKay, Sorption of dyes and copper ions onto biosorbents, *Process Biochem.* 38 (2003) 1047–1061.
- [36] Y.S. Ho, C.C. Chiang, Sorption studies of acid dye by mixed sorbents, *Adsorption* 7 (2001) 139–147.
- [37] F.C. Wu, R.L. Tseng, R.S. Juang, Adsorption of dyes and humic acid from water using chitosan-encapsulated activated carbon, *J. Chem. Technol. Biotechnol.* 77 (2002) 1269–1279.
- [38] R. Gündoğan, B. Acemioğlu, M.H. Alma, Copper (II) adsorption from aqueous solution by herbaceous peat, *J. Colloid Interf. Sci.* 269 (2) (2004) 303–309.
- [39] M. Uğurlu, A. Gürses, Ç. Doğan, M. Yalçın, Removal of phenolic and lignin compounds from bleached kraft mill effluent by fly ash and sepiolite, *Adsorption* 11 (2005) 87–97.
- [40] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* 89 (1963) 31–60.
- [41] C.K. Jain, M.K. Sharma, Adsorption of cadmium on bed sediments of River Hindon: adsorption models and kinetics, *Water Air Soil Pollut.* 137 (2002) 1–19.
- [42] M. Basibuyuk, C.F. Forster, An examination of the adsorption characteristics of a basic dye (Maxilon Red BI-N) on to live activated sludge system, *Process Biochem.* 38 (2003) 1311–1316.
- [43] R. Sivaraj, C. Namasivayam, K. Kadirvelu, Orange peel as an adsorbent in the removal of acid Violet 17 (acid dye) from aqueous solutions, *Waste Manage.* 21 (2001) 105–110.
- [44] G. Atun, G. Hisarli, W.S. Sheldrick, M. Muhler, Adsorptive removal of methylene blue from colored effluents on fuller's earth, *J. Colloid Interf. Sci.* 261 (2003) 32–39.
- [45] A. Gürses, S. Karaca, Ç. Dogar, R. Bayrak, M. Açıkıldız, M. Yalçın, Determination of adsorptive properties of clay/water system: methylene blue sorption, *J. Colloid Interf. Sci.* 269 (2) (2004) 310–314.
- [46] M.J. Rosen, *Surfactants and Interfacial Phenomena*, 1st ed., John Wiley & Sons, Inc., New York, 1978.
- [47] G. McKay, V. Poots, Kinetics and diffusion processes in color removal from effluent using wood, *J. Chem. Technol. Biotechnol.* 30 (1986) 279–282.
- [48] C. Lee, K. Low, S. Chow, Chrome sludge as an adsorbent for color removal, *Environ. Technol.* 17 (9) (1996) 1023–1028.
- [49] M. Alaya, M. Hourieh, A. Youssef, F. El-Sejarah, Adsorption properties of activated carbons prepared from olive stones by chemical and physical activation, *Adsorp. Sci. Technol.* 18 (1) (1999) 27–42.
- [50] C. Sainz-Diaz, A. Griffiths, Activated carbon from solid wastes using a pilot-scale batch flaming pyrolyser, *Fuel* 79 (2000) 1863–1871.
- [51] C. Woolard, J. Strong, C. Erasmus, Evaluation of the use of modified coal ash as a potential sorbent for organic waste streams, *Appl. Geochem.* 17 (8) (2002) 1159–1164.
- [52] G. Annadurai, R. Juang, D. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, *J. Hazard. Mater.* 92 (3) (2002) 263–274.
- [53] Y. Lin, H. Teng, Mesoporous carbons from waste tire char and their application in wastewater discoloration, *Micropor. Mesopor. Mater.* 54 (2002) 167–174.
- [54] D. Mohan, K.P. Singh, G. Singh, K. Kumar, Removal of dyes from wastewater using fly ash, a low-cost adsorbent, *Ind. Eng. Chem. Res.* 41 (2002) 3688–3695.
- [55] F. Banat, S. Al-Asheh, L. Al-Makhadmeh, Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters, *Process Biochem.* 39 (2003) 193–202.
- [56] M.A.M. Lawrence, R.K. Kukkadapu, S.A. Boyd, Adsorption of phenol and chlorinated phenols from aqueous solution by tetramethylammonium and tetramethylphosphonium exchanged montmorillonite, *Appl. Clay Sci.* 13 (1998) 13–20.