

This article was downloaded by:

On: 15 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Chemistry and Ecology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455114>

Physicochemical aspects of using natural scavengers in removing methylene blue (basic dye) from solution

S. M. Sirry^a; M. E. Soltan^a

^a Chemistry Department, Faculty of Science, South Valley University, Aswan, Egypt

To cite this Article Sirry, S. M. and Soltan, M. E.(2004) 'Physicochemical aspects of using natural scavengers in removing methylene blue (basic dye) from solution', *Chemistry and Ecology*, 20: 6, 449 – 458

To link to this Article: DOI: 10.1080/02757540412331304207

URL: <http://dx.doi.org/10.1080/02757540412331304207>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

PHYSICOCHEMICAL ASPECTS OF USING NATURAL SCAVENGERS IN REMOVING METHYLENE BLUE (BASIC DYE) FROM SOLUTION

S. M. SIRRY and M. E. SOLTAN*

Chemistry Department, Faculty of Science, Aswan 81528, South Valley University, Egypt

(Received 16 April 2004; In final form 19 July 2004)

Effluent from dyeing and finishing processes is an important source of water pollution. The effectiveness of bentonite, kaolinite and sediment from a local deposit in removing methylene blue as a cationic dye from aqueous solutions has been investigated. The adsorption equilibrium (isotherm) has been determined according to Freundlich and Langmuir equations. The optimum amount is 0.5 g for all adsorbents, and the optimum pH ranges are 2–8 for bentonite and 2–6 for kaolinite and sediment. With respect to kinetic modelling, the adsorption of methylene blue on various adsorbents was fitted to a second-order equation. Also, the thermodynamic parameters were determined. The negative free energy values indicate the feasibility of the process and spontaneous nature of adsorption. The positive ΔH° values indicate the endothermic nature of the process. Thus, Egyptian clay minerals and sediments have a great tendency to remove the dye from solutions.

Keywords: Kaolinite; Bentonite; Sediment; Methylene blue; Adsorption; Kinetic and thermodynamic parameters

1 INTRODUCTION

Effluents from the dyestuff manufacturing and other similar industries are generally highly coloured with a large amount of suspended organic acids and hence they are important sources of water pollution (Kannan and Sundaram, 2001). These dyes are generally toxic in nature, consume dissolved oxygen, and thus have a negative effect on aquatic life. Soil particles including clay minerals can interact with the pollutants and therefore play a role in scavenging pollutants from the environment. The adsorption properties may play an effective role in scavenging inorganic and organic pollutants from water. Minute amounts of organic dyes in water are considered very important because besides possible harmful effects, the colour in water is aesthetically unpleasant. The clays in soil can act as a natural scavenger in removing colour from contaminated water. Methylene blue contains a negatively charged chloride ion and a large positively charged ion (Drever, 1997), and replaces natural cations of clay irreversibly, as indicated by Tailor (1985). In the present study, an aqueous solution of a basic dye, methylene blue, was used as a model compound in an attempt to determine the adsorption capacity of bentonite, kaolinite and sediment.

* Corresponding author. E-mail: mesoltan@hotmail.com

The adsorbent properties of these clay materials were compared by means of a batch liquid-phase adsorption test. Solutions containing methylene blue were shaken with the prepared adsorbent in a water bath shaker. The influences of (1) adsorbent dose, (2) concentration of methylene blue, (3) pH of the medium, (4) effect of time, and (5) effect of temperature on the adsorption are investigated.

2 EXPERIMENTAL

2.1 Sampling

Bentonite (a sodium salt of montmorillonite octahedral aluminosilicate, 58.25% SiO₂, 18.48% Al₂O₃, 7.3% Fe₂O₃, 2.25% Na₂O, 2.62% MgO, 2.07% CaO and 1.2% K₂O) and kaolinite (Al₂Si₂O₅(OH)₄ containing 39.5% Al₂O₃, 46.55% SiO₂ and 13.9% H₂O) samples were collected from the Allaqi and Kalabsha regions, south of Aswan, Egypt. Sediment sample (clay size fraction containing 34.6% montmorillonite, 34.2% kaolinite, 17.8% illite and 13.6% quartz) was collected from the main stream of river Nile at Abu-El Riesha village, north of Aswan, Egypt. The samples were dried at 105 °C in an electric oven for 48 h, powdered in an agate mortar, then sieved through a <63 μm sieve.

2.2 Adsorption Studies

The adsorption of methylene blue was carried out in a batch process by varying the amount (4–40 g l⁻¹), adsorptive concentration (1–120 mg l⁻¹), pH (2.0–10) of medium, equilibrium time (5–300 min) and temperature (30 and 50 °C). The mixture, in a 100 ml conical flask, was shaken in a water bath shaker (Kottermann, Uetex–Hanigsely, Germany). The pH was adjusted by adding a few drops of dilute NaOH or HCl before shaking. The mixture was then allowed to settle. The methylene blue concentration in the supernatant was determined using a spectrophotometer (Shimadzu 160). The adsorbed dye concentrations were calculated by the difference between the initial concentration and non-adsorbed concentration.

2.3 Equilibrium and Kinetic Modelling

Methylene blue adsorption isotherm data, when starting at different initial concentrations, have been fitted to the models of Langmuir and Freundlich. These data were obtained by the methylene blue concentration measurement after adsorbent/adsorbate contact periods equal to the equilibrium times which were previously determined in adsorption kinetic studies. The well-known expression of the Langmuir model is:

$$q_{\text{eq}} = \frac{Q^{\circ} b C_{\text{eq}}}{1 + b C_{\text{eq}}} \quad (1)$$

with q_{eq} (mg g⁻¹) representing the amount of adsorbed methylene blue per unit weight of the corresponding adsorbent and C_{eq} (mg l⁻¹) being unadsorbed dye concentration in solution, both at equilibrium. Q° (mg g⁻¹) is the maximum amount of methylene blue per unit weight of adsorbent to form a monolayer on the surface bond, and b (l mg⁻¹) is a constant related to the affinity of binding sites (Juang *et al.*, 1997).

The Freundlich equation is:

$$q_{\text{eq}} = K_{\text{F}} C_{\text{eq}}^{1/n} \quad (2)$$

where K_{F} and n are the Freundlich constants characteristic of the system, also being an indicator of adsorption capacity and adsorption intensity, respectively.

A simple kinetic analysis of adsorption is the pseudo-first-order equation (Sarkar and Chatteraj, 1993; Tutem *et al.*, 1998):

$$\frac{dq}{dt} = k_1(q_{\text{eq}} - q_t), \quad (3)$$

where k_1 is the rate constant of pseudo-first-order adsorption, and q_e denotes the amount of adsorption at equilibrium. After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Equation 3 becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t, \quad (4)$$

where the value of q_e must be obtained independently from equilibrium experiments. However, a pseudo-second-order equation based on adsorption capacity may be expressed in the form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \quad (5)$$

where k_2 is the rate constant of pseudo-second order adsorption (Ho and McKay, 2000). By integrating Equation 5 and applying initial conditions, we have the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t. \quad (6)$$

Hence, k_2 and q_e in Equation 6 can be obtained from the intercept and slope of the plot of (t/q_t) vs. t .

2.4 Thermodynamic Parameters of the Adsorption

The thermodynamic parameters of the adsorption process are obtained from experiments at two temperatures (30 and 50 °C) using the following equations (Khan *et al.*, 1995; Singh and Srivastava, 1999)

$$(1) \log K_{\text{d}} = \Delta^\circ S / (2.303R) - \Delta H^\circ / 2.303RT$$

$$(2) \Delta G^\circ = -RT \ln k$$

$$(3) \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where K_{d} is the distribution coefficient for the adsorptive and is equal to the ratio of amount adsorbed (mg g^{-1}) to the adsorptive concentration (mg l^{-1}).

3 RESULTS AND DISCUSSION

3.1 Effect of Adsorbent Dose and Methylene Blue Concentrations

In all cases, the percentage of dye adsorbed increases with an increasing of amount but decreases at an amount equal to 40 g l^{-1} due to the decreasing equilibrium concentration of the dye (Tab. I).

The removal efficiency of methylene blue decreases with increasing initial concentration of the dye against the constant dose of adsorbents (Tab. II). This is due to the lack of available active sites required for the high initial concentrations of methylene blue (Kannan and Sundaram, 2001). Sediment and bentonite exhibit a higher removal efficiency than kaolinite (Tab. II). The bentonite has a higher adsorption efficiency than kaolinite because of its larger surface area. The surface layer of bentonite contains a tetrahedron of four oxygen atoms surrounding a central cation, Si^{4+} , while the surface layer of kaolinite contains an octahedron of six oxygens (or hydroxyls) around a large cation, which is most commonly Al^{3+} (Tinsley, 1979). The washed clay minerals (sediment) have regenerative sites to adsorb the pollutants with a high efficiency (Soltan *et al.*, 2001).

3.2 Effect of pH

The adsorption efficiency according to the effect of pH was determined for different adsorbents using a constant amount (20 g l^{-1}) and a known initial concentration of dye (40 mg l^{-1}). The removal efficiency was studied in the pH range (2–10) using HCl or NaOH solution. Acid or alkali attack induces marked changes in the crystal structure of aluminosilicate minerals due to dissolution of structural ions and/or rearrangement of the structure (Jozefaciuk and Bowanko, 2002). Maximum adsorption of methylene blue (99.53 and 98.37%) occurred at pH 8 on the surface of sediment and bentonite, respectively. Kaolinite sample exhibited moderate removal (63.70%) at pH 7.

Generally, all adsorbents exhibited good results against methylene blue adsorption over a wide range of pH values (Tab. III). High adsorption efficiency of the different adsorbents as a result of all adsorbents are considered as clay minerals. The increased adsorption under basic conditions may be related to the preference of the dye cations for basic sites (Ghosh and Bhattacharyya, 2002). More pronounced structural changes of bentonite were observed by Ruiz *et al.* (1997), who found that the laminar structure of the starting material was converted into spherical units of the zeolitic nature by alkaline treatment in distilled and seawater media. The increase in uptake of the dye with increasing pH is normally attributed to

TABLE I Percentage of adsorption of methylene blue ($[\text{MB}]_{\text{tot}} = 40 \text{ mg l}^{-1}$) with different amounts of bentonite, kaolinite and sediment.

Amount (g l^{-1})	% Adsorption		
	Bentonite	Kaolinite	Sediment
4	98.51	58.05	98.1
8	98.77	60.21	99.33
12	98.96	61.43	99.33
16	99.15	62.53	99.33
20	99.24	63.50	99.53
24	99.91	62.53	99.53
32	99.90	62.44	99.50
40	99.81	60.15	99.43

TABLE II Removal efficiency (%) of methylene blue using different adsorbents according to initial concentrations of dye (mg l^{-1}), constant amount (20 g l^{-1}) and pH medium = 8.

Initial concentration (mg l^{-1})	Efficiency (%)		
	Bentonite	Kaolinite	Sediment
1	100	100	100
2	100	100	100
5	100	95.60	100
10	100	78.30	100
20	100	65.40	100
40	98.37	63.90	99.53
60	97.10	60.60	99.42
100	74.10	60.30	99.35
120	60.40	52.10	80.10

increased association of the dye cations by the dissociation of methylene blue, with a negatively charged kaolin surface at an increasingly higher pH (Singh and Srivastava, 1999). Because of the complex changes in minerals in acid or alkaline environments, their surface properties are modified. All elements except Si dissolved better in acidic than in alkaline media. However, excluding biotite and vermiculite, the total amount of dissolved solid was greater in 5 N NaOH than in 5 N HCl, due to extreme Si dissolution (Jozefaciuk and Bowanko, 2002). Dekany *et al.* (1999) observed that as the amount of elements extracted from the material increased, the specific surface area of the sample also increased. Cleaning and disaggregation of the particles and the increase in the number of micropores were responsible for the increase in specific surface area.

3.3 Adsorption Isotherms

Methylene blue adsorption on bentonite, kaolinite and sediment can be described by the Freundlich equation (Figs. 1–3 and Tab. IV). The Freundlich exponent, n , between 0.057 and 0.24 indicates favourable adsorption ($0 < n < 1$). The equilibrium data obtained for methylene blue indicate that the bentonite has the highest adsorption capacity, whereas kaolinite has a moderate capacity, and sediment has the lowest. The results obtained were not fitted to the linearized adsorption isotherms of Langmuir.

TABLE III Effect of pH on the adsorption efficiency (%) of methylene blue on the surface of different adsorbents.

pH	Adsorbent		
	Bentonite	Kaolinite	Sediment
2	85.33	60.85	96.05
4	80.19	60.95	96.13
6	91.15	61.25	97.12
7	97.88	63.70	98.75
8	98.37	63.50	99.53
10	95.13	61.59	99.15

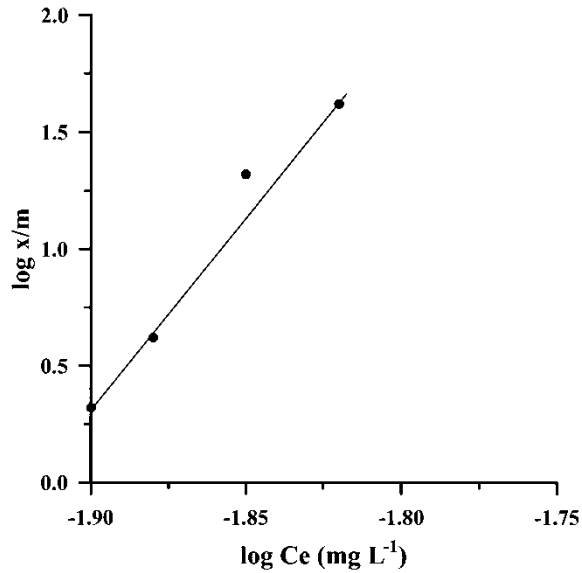


FIGURE 1 Freundlich plots for the adsorption of methylene blue by bentonite at room temperature.

3.4 Kinetics of Adsorption

The effect of contact time on the amount of dye adsorbed was investigated (Tab. V). The extent of adsorption of methylene blue by bentonite was very rapid, and the methylene blue was removed completely from the solution after 15 min, whereas in the case of kaolinite and sediment, the equilibrium was attained after 5 and 2 h, respectively. In the batch type of adsorption, a monolayer of adsorbate is normally formed on the surface of the adsorbent (Weber, 1972), and the rate of removal of adsorbate species from aqueous solution is

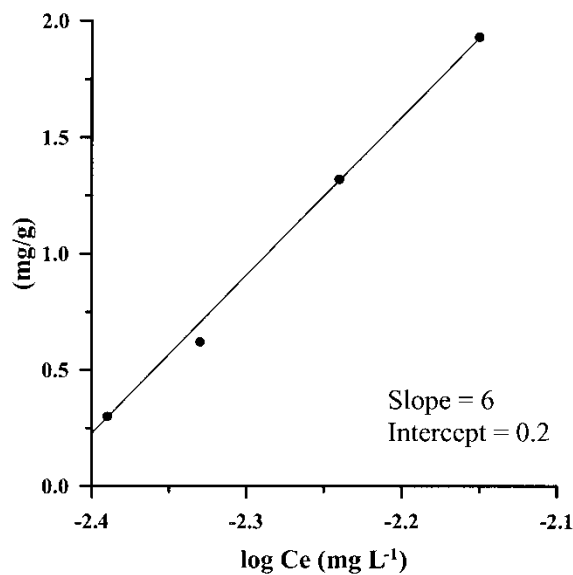


FIGURE 2 Freundlich plots for the adsorption of methylene blue by kaolinite at room temperature.

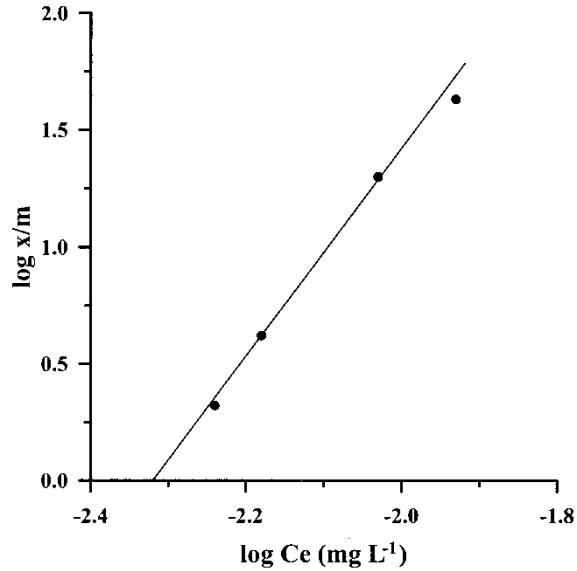


FIGURE 3 Freundlich plots for the adsorption of methylene blue by sediment at room temperature.

TABLE IV Freundlich parameters of adsorption isotherms.

Clays	$n \text{ (mg g}^{-1}\text{)}$	$k \text{ (mg g}^{-1}\text{)}$
Bentonite	0.057	2.10
Kaolinite	0.17	1.58
Sediment	0.24	0.473

controlled primarily by the rate of transport of adsorbate species from the exterior sites to the interior sites of the adsorbate particle (Weber and Morris, 1964). The amount derived from the first-order rate equation does not fit well for the whole range of contact times (Tab. VI). However, the second-order kinetic equation gives a linear relation in the case of kaolinite and sediment (Fig. 4 and Tab. VII). This is in agreement with an adsorption mechanism

TABLE V Amount of adsorbed methylene blue (q_t) at different times. ([MB] = 84.47 mg/25 ml, bentonite; 12.67 mg/25 ml, kaolinite and 105.59 mg/25 ml, sediment.

Time (min)	$q_t \text{ (mg g}^{-1}\text{)}$		
	Bentonite	Kaolinite	Sediment
5	168.940	18.663	210.978
15	168.952	18.823	210.986
30	168.952	19.903	211.040
60	168.952	19.402	211.108
120	168.952	22.003	211.130
180	168.952	23.370	211.132
240	168.952	24.713	211.134
300	168.952	25.100	211.134

TABLE VI Kinetic models for adsorption of methylene blue on kaolinite and sediment.

Time (min)	$\log(q_e - q_t)$		q_t	
	Kaolinite	Sediment	Kaolinite	Sediment
5	0.823	-0.80	0.27	0.024
15	0.812	-0.82	0.80	0.07
30	0.806	-1.027	1.59	0.14
60	0.772	-1.50	3.09	0.28
120	0.520	-2.40	5.45	0.57
180	-1.960	-	7.70	0.85

being the rate-controlling step (Mckay and Ho, 1999a, b). The adsorption of methylene blue on bentonite is too rapid to be followed kinetically.

The second-order rate constant (K_{2a}) and q_{eq} values were determined from the slope and intercepts of the plots. The results are shown in Table VI and Figures 1 and 5. The rate of adsorption (K_{ad}) is found to be high in the sediment ($8.9 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$) and low in kaolinite. The $q_{eq,cal}$ obtained agreed very well with the experimental $q_{eq,exp}$.

3.5 Thermodynamic Parameters

The values of $\log k_d$ and thermodynamic parameters ΔG° , ΔH° and ΔS° at 30 and 50°C are listed in Table VIII. Three main thermodynamic properties include the enthalpy of adsorption (ΔH°), free energy change (ΔG°) due to transfer of unit mole of solute from solution to the solid-liquid interface and entropy (ΔS°) of adsorption. The negative free energy values indicate the feasibility of the process and spontaneous nature of adsorption (Mall and Upadhyay, 1995, 1998). The amount of adsorption increase with temperature and the positive ΔH° values indicate the endothermic nature of the process, and this process is due to chemical bond or chemisorption. The endothermic nature of the adsorption of methylene

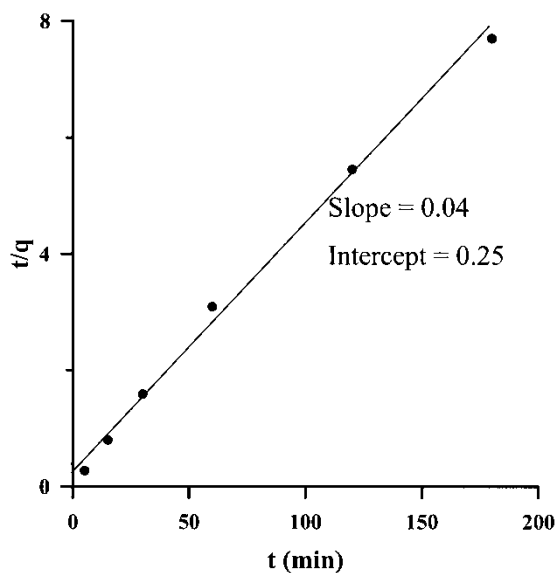


FIGURE 4 Second-order kinetic equation for the adsorption of methylene blue on kaolinite.

TABLE VII Second-order rate constants of kaolinite and sediment adsorbent.

Adsorbent	$K_{2ad} \times 10^{-3} (g\ mg^{-1}\ min^{-1})$	$q_{eq} (mg\ g^{-1})$
Kaolinite	6.4	25.00
Sediment	8.9	211.86

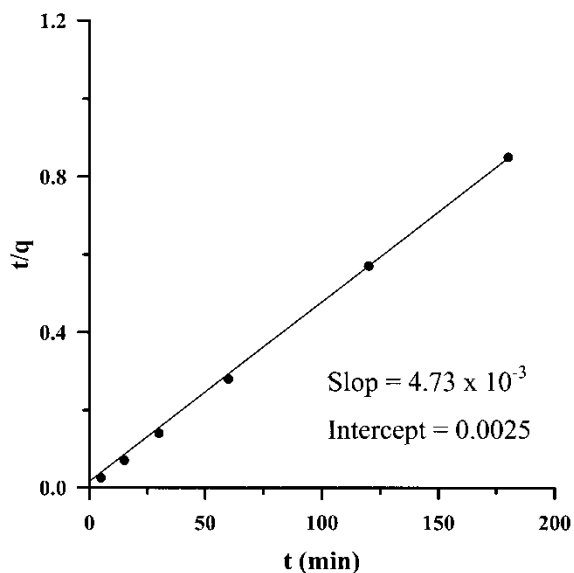


FIGURE 5 Second-order kinetic equation for the adsorption of methylene blue on sediment.

TABLE VIII Thermodynamic parameters for adsorption of methylene blue on various adsorbents.

Adsorbent	$\log K_d$		$-\Delta^\circ G (kJ\ mol^{-1})$		Mean ΔH° ($kJ\ mol^{-1}$)	Mean ΔS° ($kJ\ mol^{-1}$)
	$30^\circ C$	$50^\circ C$	$30^\circ C$	$50^\circ C$		
Bentonite	3.931	4.100	32.75	25.31	17.0	0.13
Kaolinite	1.317	1.324	7.63	8.17	0.70	0.03
Sediment	2.990	3.145	17.31	19.41	15.5	0.11

blue was previously observed by De and Basu (1999) and also by Ghosh and Bhattacharyya (2002). The positive values of standard entropy change ($\Delta^\circ S$) indicate the increase in disturbance during the adsorption process. An entropy increase was also observed by other workers, as pointed out above.

4 CONCLUSION

Egyptian clay minerals and Nile sediment have a great tendency to remove dye from solutions. The removal process is very rapid and spontaneous. These naturally occurring adsorbents may be used for any dye pollutant. According to the Freundlich equation, bentonite has

the highest capacity for adsorption. The effect of contact time supported the efficiency of bentonite as an excellent adsorbent, where the extent of adsorption of methylene blue by bentonite was very rapid. The sediments of the river Nile have a greater potential for the removal of dye in acidic and basic medium by adsorption mechanisms.

References

- De, D. S. and Basu, J. K. (1999). Adsorption of methylene blue onto a low cost adsorbent developed from sawdust. *Indian Journal of Environmental Protection*, **19**, 416–421.
- Dekany, I., Turi, L., Fonseca, A. and Nagy, J. B. (1999). The structure of acid treated sepiolites: small-angle X-ray scattering and multi MAS–NMR investigations. *Applied Clay Science*, **14**, 141–160.
- Drever, J. I. (1997). *The Geochemistry of Natural Waters*. Prentice Hall, Englewood Cliffs, NJ.
- Ghosh, D. and Bhattacharyya, K. G. (2002). Adsorption of methylene blue on kaolinite. *Applied Clay Science*, **20**, 295–300.
- Ho, Y. S. and McKay, G. (2000). The kinetic of sorption of divalent metal ions onto sphagnum moss peat. *Water Research*, **34**, 735–742.
- Jozefaciuk, G. and Bowanko, G. (2002). Effect of acid and alkali treatments on surface areas and adsorption energies of selected minerals. *Clays and Clay Minerals*, **50**, 771–783.
- Juang, R. S., Tseng, R. L., Wu, F. C. and Lee, S. H. (1997). Adsorption behavior of reactive dye from aqueous solution on chitosan. *Journal of Chemical Technology and Biotechnology*, **70**, 391–399.
- Kannan, N. and Sundaram, M. M. (2001). Kinetics and mechanism of removal of methylene blue by adsorption on various carbons a comparative study. *Dyes and Pigments*, **51**, 25–40.
- Khan, S. A., Rehman, R. and Khan, M. A. (1995) Adsorption of Cr(III), Cr(VI) and Ag(I) on bentonite. *Waste Management*, **15**, 271–282.
- McKay, G. and Ho, Y. S. (1999a). Pseudo second order model for sorption process. *Process Biochemistry*, **34**, 451–465.
- McKay, G. and Ho, Y. S. (1999b). The sorption of lead (II) on peat. *Water Research*, **33**, 578–584.
- Mall, I. D. and Upadhyay, S. N. (1995). Removal of basic dyes from wastewater using boiler bottom ash. *Indian Journal of Environmental Health*, **37**, 1–10.
- Mall, I. D. and Upadhyay, S. N. (1998). Studies on treatment of basic dyes bearing wastewater by adsorption treatment using fly ash. *Indian Journal of Environmental Health*, **40**, 177–188.
- Ruiz, R., Blanco, C., Pesquera, C., Gonzalez, F., Benito, I. and Lopez, J. L. (1997). Zeolitization of a bentonite and its application to the removal of ammonium ion from waste water. *Applied Clay Science*, **12**, 73–83.
- Sarkar, D. and Chatteraj, D. K. (1993). Activation parameters for kinetics of protein adsorption at silica–water interface. *Journal of Colloid and Interface Science*, **157**, 219–226.
- Singh, D. K. and Srivastava, B. (1999). Removal of basic dye from aqueous solutions by chemically treated Psidium Guyava leaves. *Indian Journal of Environmental Health*, **41**, 333–345.
- Soltan, M. E., Rashed, M. N. and Taha, G. M. (2001). Heavy metal levels and adsorption capacity of Nile river sediments. *International Journal of Environmental Analytical Chemistry*, **80**(3), 167–186.
- Taylor, R. K. (1985). Cation exchange in clay and mud rock by methylene blue. *Journal of Chemical Technology and Biotechnology*, **35A**, 195–207.
- Tinsley, I. J. (1979). *Chemical Concepts in Pollutant Behaviour*. John Wiley & Sons, New York.
- Tutem, E., Apak, R. and Unal, G. F. (1998). Adsorptive removal of chlorophenols from water by bituminous shale. *Water Research*, **32**, 2315–2324.
- Weber, W. J. (1972). *Physico-Chemical Processes for Water Quality Control*. Wiley InterScience, New York.
- Weber, W. J. and Morris, J. C. (1964). Removal of biologically resistant pollutants from wastewater by adsorption. In: Eckenfelder W. W. (ed.), *Advances in Water Pollution Research*. Pergamon, Oxford.