ELSEVIER

Journal of Hazardous Materials B134 (2006) 144–148

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Adsorption of herbicide paraquat by clay mineral regenerated from spent bleaching earth

Wen-Tien Tsai *, Chi-Wei Lai

Department of Environmental Engineering and Science, Chia Nan University of Pharmacy and Science, Tainan 717, Taiwan

Received 22 November 2004; received in revised form 21 October 2005; accepted 24 October 2005

Abstract

The adsorption of herbicide paraquat (as model adsorbate) in aqueous solution onto regenerated clay mineral from bleaching earth waste has been studied in a batch reaction system. The adsorption rate has been investigated under the controlled process parameters including initial pH, salinity and temperature. Based on the high affinity between cationic paraquat and clay mineral, a pseudo-second order model has been developed using experimental data to predict the rate constant of adsorption, and equilibrium adsorption capacity. The results showed that the adsorption process could be satisfactorily described with the reaction model and were reasonably explained by assuming a competitive adsorption mechanism in the ion exchange process. Further, the fitted adsorption capacity at equilibrium decreased with increasing temperature. It implied that the strong interaction might play an important role in the paraquat–clay system. Overall, the results from this study demonstrated that the clay resource regenerated from bleaching earth waste could be used as a low-cost mineral adsorbent for the removal of environmental cationic organic pollutants from the aqueous solution.

Keywords: Liquid-phase adsorption; Paraquat; Regenerated bleaching earth; Kinetic modeling

1. Introduction

Organic pesticide residues have been reported in drinking water, agricultural water and groundwater [1–3]. These pesticides generally penetrate into surface water in runoff from land applications [4] and from industrial wastewater discharges [5,6]. For example, it was reported that the maximum concentration of paraquat in the untreated wastewater was close to 40 mg/L (i.e., 155.5 μmol/L). The mobility of pesticide left in soil, on the other hand, generally enters groundwater via leaching [4]. Paraquat (1,1′-dimethyl-4,4′-bipyridylium chloride), which was extensively used as a non-selective herbicide, is one of the bipyridinium compounds [7]. However, it is well known that this compound is also one of the most acutely toxic compounds because it has caused many cases of human poisoning, with the lung being the primary target tissue [8]. The maximum contaminant level (MCL) of paraquat has been set at 0.01 mg/L (i.e., 0.039 μmol/L) according to the Drinking Water Standard in Taiwan [9]. Also, paraquat residue limits in foods have been recently amended to 0.2 mg/kg (i.e., 0.78 μmol/L) [10]. Consequently it is important to study the adsorption behavior of cationic paraquat with clay minerals from the viewpoints of mobility in soil and/or methods of control in the adsorption process.

Bleaching earths refer to clay minerals used in their natural states or after acid- and heat-activation (i.e., activated bleaching earth) [11]. They have the capacity to adsorb coloring matters and undesirable residues from oils, mainly applied in the bleaching process of edible oils [12]. Spent bleaching earth (SBE) mainly generated from the edible oil processing industry is thus an industrial waste. The waste was commonly disposed of to landfill without any pretreatment. Due to the industrial waste management and resource conservation, the utilization of this food processing waste has recently increased in response to low-cost alternatives to activated carbon [13–16]. It was concluded from adsorption studies that the regenerated bleaching earth could be an effective adsorbent for removing hazardous organic pollutants such as paraquat and organic dyes [13–16]. The maximum adsorption capacities of basic dyes were found to be obviously larger than those of acid dyes and reactive dyes,

---

* Corresponding author. Tel.: +886 6 2660393; fax: +886 6 2669090.
E-mail address: wwtsai@mail.chna.edu.tw (W.-T. Tsai).

0304-3894/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2005.10.045

possibly due to the negatively charged surface of regenerated SBE, which poses higher affinity for these cationic dyes.

In our previous studies [17–19], we found a rapid decrease in residual paraquat concentration within 10 min from the results of adsorption kinetics using activated bleaching earth. With respect to the kinetics and its modeling of paraquat adsorption onto adsorbent from the aqueous solution, other published information is limited [20]. The present study aimed at providing one option for utilizing the clay resource in the water treatment applications and determining the potential mobility of the toxic compound in the soil-simulated environment. Thus, the main objectives of this work were to determine the extent of the effects of pH, salinity and temperature at paraquat adsorption rate, and also evaluate the usefulness of pseudo-second order model for analyzing the adsorption system.

2. Materials and methods

2.1. Materials

The model adsorbate used in the kinetic experiments is paraquat ($C_{12}H_{14}Cl_2N_2$, formula weight = 257.2) with purity of >99%, which was purchased from Sigma Chemical Co. (USA). The chemical properties and mineralogy of spent bleaching earth were measured by elemental analysis/FTIR and X-ray powder diffraction (XRD), respectively [21]. The contents of C, H and N of the precursor are 26.2, 4.3 and 0.4 wt%, respectively. From the FTIR spectra and XRD, the surface nature is associated with the presence of structural water within the montmorillonite matrix, along with the presence of silicate matrix and silica/quartz. Regenerated bleaching earth employed as the clay adsorbent in the present study was prepared in the activation conditions of constant ramp rate of 10 °C/min under N_2 flow of 0.3 L/min and CO_2 flow of 0.3 L/min at activation temperature of 800 °C and holding time of 2 h [15]. Its main physical properties are given as follows: BET surface area 101.5 m^2/g, total pore volume 0.204 cm^3/g, average pore diameter 8.04 nm, real (true) density 1.825 g/cm^3, particle density 1.330 g/cm^3 and particle porosity 0.271. Obviously, the adsorbent is characteristic of mesoporous structure. H_2SO_4 and NaOH with purity of minimum 95.0% and 99.0%, respectively, used for adjusting initial pH value of aqueous solution, were purchased from Merck Co. (Germany) and Wako Chemical Co. (Japan), respectively. Common chloride salts (i.e., LiCl, NaCl, and KCl) with purities of minimum 98.0%, purchased from Kanto Chemical Co. (Japan), were used to investigate the effect of solution salinity on adsorption kinetics of paraquat.

2.2. Adsorption kinetics

All the experiments of adsorption kinetics were carried out in a ca. 3-L stirred batch adsorber with four baffles as similarly described in our previous studies [17–19]. The adsorber was immersed in a refrigerated circulating-water bath for isothermal conditioning prior to the experiment. Preliminary investigations on the adsorption rate using the clay adsorbent have indicated that the process occurred rapidly. After the lapse of 60–120 min, a gradual approach to the adsorption capacity was observed. The effect of agitation speed ranging from 200 to 600 rpm on paraquat adsorption seemed to be negligible. Thus, each sample of the solution (ca. 15 mL) was withdrawn from the adsorber by using a 20-mL syringe at intervals of 0.5, 1.0, 2.0, 5.0, 10.0, 30.0, 60.0 and 120.0 min. It was then filtrated with a fiber membrane (Cat. No.: A045A025A; ADVANTEC MFS Inc.). The analyses of concentration of paraquat in the filtrate paraquat solution after adding sodium dithionite were immediately made with a 1.0-cm light path quartz cell in a spectrophotometer (Shimadzu UV-1201) at λ_{max} of 600 nm [22]. The amount of paraquat adsorbed was determined by the difference between the initial and liquid-phase concentrations of paraquat solution at t time (mg/L), respectively. The effects of initial pH (i.e., 3.0, 7.0 and 11.0), salinity (i.e., 0, 0.05, 0.5 and 2.5 M of NaCl, 0.5 M of LiCl and 0.5 M of KCl) and temperature (i.e., 15, 25, 35 and 45 °C) on the adsorption kinetics were investigated under the initial concentration of 30 mg/L of paraquat, adsorbent dosage of 0.5 g/2 L and agitation speed of 400 rpm. In order to evaluate the statistical significance of data in the kinetic experiments, a preliminary experiment was repeated using identical conditions, showing that the reproducibility of the measurements is within 5%.

3. Results and discussion

3.1. Pseudo-second order reaction model

The rapid decrease in residual paraquat concentration within a short time scale implied a strong cation-exchange interaction between the negatively charged surface and divalent paraquat. Consequently a simple kinetic analysis of adsorption, pseudo-second order equation, was thus used to fit the experimental data and describe the adsorption system in the present work. The differential rate equation is the following form [23–25]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{1}$$

where k is the rate constant of sorption (g/mg min), q_e the amount of paraquat ion adsorbed at equilibrium (mg/g) and q_t is the amount of paraquat ion adsorbed at any time t (mg/g). The linear form of the diffusion equation gives:

$$\frac{t}{q_t} = \frac{1}{k \cdot {q_e}^2} + \frac{1}{q_e} \cdot t \tag{2}$$

Rate parameters, k and q_e, can be directly obtained from the intercept and slope of the plot of t/q_t against t. The equilibrium concentration (i.e., C_e) can be further calculated using the mass balance concept as the value of q_e has been obtained from the fitting of Eq. (2).

3.2. Effect of initial pH

The effect of the initial pH (i.e., 3.0, 7.0 and 11.0) on the paraquat uptake rate by the regenerated clay adsorbent is shown in Fig. 1 where the experimental data are denoted as discrete points and those obtained from the model by solid lines. From Fig. 1, it is evident that the rate of adsorption decreased with

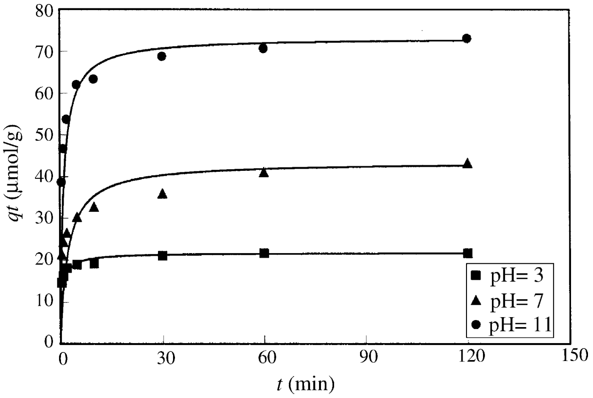

Fig. 1. Plots of adsorbed paraquat amount vs. time at various initial pH (initial concentration = 30 mg/L (i.e., 116.6 μmol/L), adsorbent dosage = 0.5 g/2L, agitation speed = 400 rpm and temperature = 25 °C; symbols: experimental data, full lines: calculated from Eq. (2) and Table 1).

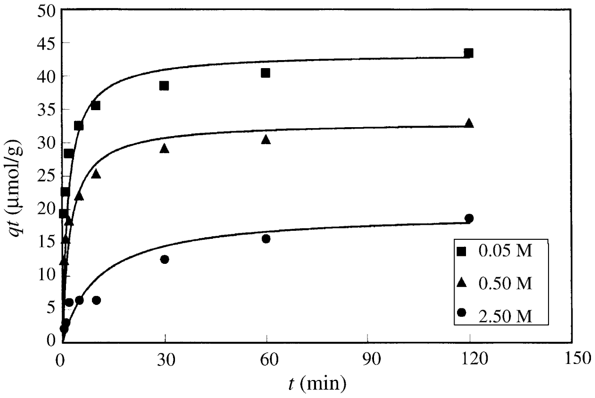

Fig. 2. Plots of adsorbed paraquat amount vs. time at various NaCl concentrations (initial concentration = 30 mg/L (i.e., 116.6 μmol/L), adsorbent dosage = 0.5 g/2 L, initial pH 11.0, agitation speed = 400 rpm and temperature = 25 °C; symbols: experimental data, full lines: calculated from Eq. (2) and Table 2).

time until it gradually approached a plateau due to the continuous decrease in the concentration driving force. Values of k, q_e, correlation coefficient (R^2), and C_e for the adsorption system, computed from the above equations, are listed in Table 1, from which it is evident that the adsorption kinetics of paraquat on the regenerated clay mineral follows this model with the regression coefficients of higher than 0.99 for all the systems in this study. Clearly, the adsorption capacity (i.e., q_e) increased as the initial pH and equilibrium concentration (i.e., C_e) thus decreased, and the results are consistent with the results as described before [18]. These observations indicate that as the pH increased the adsorbed amount of cationic paraquat increased in response to the increasing number of negatively charged sites that are available due to the loss of H^+ from the surface [26]. It was reported that the equilibrium amount of paraquat that can be adsorbed on illite at the same pH (i.e., 11) was proximate to 18.6 mg/g (i.e., 72.3 μmol/g) [27], which is slightly lower than 18.8 mg/g (i.e., 73.1 μmol/g) of regenerated bleaching earth as listed in Table 1. In addition, it was found that the variation of rate constant (i.e., k) seemed to have no significant trend with initial pH, which is also similar to the previous study [18].

3.3. *Effect of salinity*

The effect of varying the concentration of NaCl on paraquat adsorption rate at initial pH of 11.0 is shown in Fig. 2. The values of parameters for the adsorption system have been obtained and listed in Table 2. From the results of Table 2, it is evident that the correlation between the experimental and theoretical results is also good with high R^2 values (0.9773–0.999). It can be expected that the paraquat concentration in the solution increased and the adsorbed amount thus decreased as the concentration of NaCl increased, and the results are consistent with the previous study [14] and other works [28,29]. The presence of other cations (i.e., sodium ion) is also expected to affect paraquat adsorption onto the clay mineral due to the competitive adsorption [29,30].

3.4. *Effect of alkali metal ion*

Because ion exchange may be primarily an electrostatic process in the adsorption system, the smaller the solvated (hydrated) radius of the ion, closer it can approach the negatively charged clay surface and greater is the affinity of the surface for the ion. For the monovalent cations present at equal concentrations in solution, the order of the affinity of the clay surface is as follows [20]: $K^+ > Na^+ > Li^+$. The effect of alkali metal ion (i.e., Li^+, Na^+ and K^+) on paraquat adsorption rate at the ion concentration of 0.5 M and initial pH of 11.0 is shown in Fig. 3. From the results in Table 3, the correlation between the experiments with the theoretical results is again excellent with high R^2 values (0.9983–0.9985). The data listed in Table 3

Table 1
Kinetic parameters for paraquat adsorption onto the regenerated clay at various initial pH[a]

Initial pH	k (g/mmol min)	q_e (μmol/g)	Correlation coefficient	C_e (μmol/g)
3.0	74.8	21.7	0.9999	111.2
7.0	10.0	43.4	0.9978	105.8
11.0	12.6	73.2	0.9997	98.3

[a] Adsorption conditions: initial concentration = 30 mg/L (i.e., 116.6 μmol/L), adsorbent dosage = 0.5 g/2 L, agitation speed = 400 rpm and temperature = 25 °C.

Table 2
Kinetic parameters for paraquat adsorption onto the regenerated clay at various NaCl concentrations[a]

NaCl concentration (M)	k (g/mmol min)	q_e (μmol/g)	Correlation coefficient	C_e (μmol/g)
0.0	12.6	73.2	0.9999	98.3
0.05	12.3	43.5	0.9986	105.8
0.50	12.9	33.0	0.9985	108.4
2.50	4.9	12.9	0.9773	111.7

[a] Adsorption conditions: initial concentration = 30 mg/L (i.e., 116.6 μmol/L), adsorbent dosage = 0.5 g/2 L, initial pH = 11.0, agitation speed = 400 rpm and temperature = 25 °C.

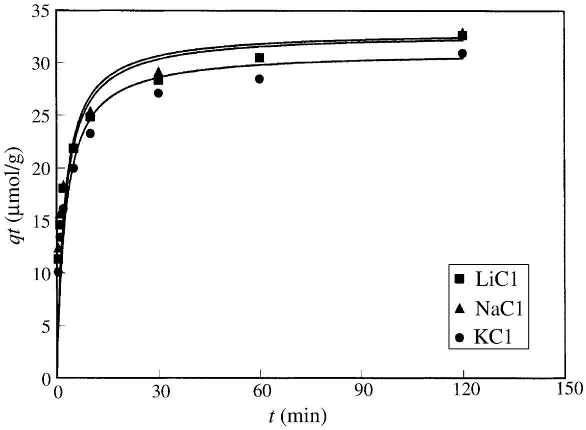

Fig. 3. Plots of adsorbed paraquat amount vs. time at various 0.5 M alkali metal ions (initial concentration = 30 mg/L (i.e., 116.6 μmol/L), adsorbent dosage = 0.5 g/2L, initial pH 11.0, agitation speed = 400 rpm and temperature = 25 °C; symbols: experimental data, full lines: calculated from Eq. (2) and Table 3).

indicate that the order of adsorption capacity (i.e., q_e) for the monovalent ions was observed as follows: Na^+ (8.50 mg/g or 33.0 μmol/L) > Li^+ (8.45 mg/g or 32.9 μmol/L) > K^+ (8.00 mg/g or 31.1 μmol/L). This result is slightly similar to the previous study [18] in that the order of adsorption capacity (i.e., q_e) for the cationic paraquat onto activated bleaching earth is as follows: Li^+ (32.79 mg/g or 127.5 μmol/L) > Na^+ (31.25 mg/g or 121.5 μmol/L) > K^+ (24.75 mg/g or 96.2 μmol/L). In the present work, the adsorption capacities of paraquat onto the regenerated bleaching earth are significantly lower than those onto activated bleaching earth at the same adsorption conditions [14], which are also in accordance with the physical properties between these two clay adsorbents (e.g., ca. 100 m^2/g versus 260 m^2/g of BET surface area, respectively).

3.5. *Effect of temperature*

The plots of q_t versus t at various temperatures of paraquat solution are shown in Fig. 4. The adsorption process still confirms to fit the pseudo-second order model with a high correlation coefficient (>0.99). Values of model parameters (i.e., k and q_e), and C_e for different temperatures have been carried out, and the results are given in Table 4. It is clear that fitted adsorption capacity at equilibrium (i.e., q_e) for each temperature increased with increasing temperature. For example, values of q_e increased from 14.60 mg/g (i.e., 56.7 μmol/L) at 15 °C to 24.80 mg/g (i.e., 96.4 μmol/L) at 45 °C. Furthermore, values of C_e decreased with increasing temperature. Values of rate constant (i.e., k), on the other hand, decrease with increasing temperature. The observations are significantly different from those studied by Hamadi et al. [20] and Nakamura et al. [31] where adsorption capacity of paraquat was found to decrease with increasing temperature in the case of activated carbon, but are in line with those of other work [32] for adsorption of basic dyes onto regenerated bleaching earth. These results imply that a chemisorption-like mechanism may play an important role in the cationic paraquat–clay adsorbent system, leading to strong binding of the cation molecules to the clay particles.

Table 3
Kinetic parameters for paraquat adsorption onto the regenerated clay at various alkali metal ions of 0.5 M[a]

Alkali metal salt	k (g/mmol min)	q_e (μmol/g)	Correlation coefficient	C_e (μmol/g)
LiCl	12.3	32.9	0.9985	108.4
NaCl	12.9	33.0	0.9985	108.4
KCl	12.1	31.1	0.9983	108.9

[a] Adsorption conditions: initial concentration = 30 mg/L (i.e., 116.6 μmol/L), adsorbent dosage = 0.5 g/2 L, initial pH 11.0, agitation speed = 400 rpm and temperature = 25 °C.

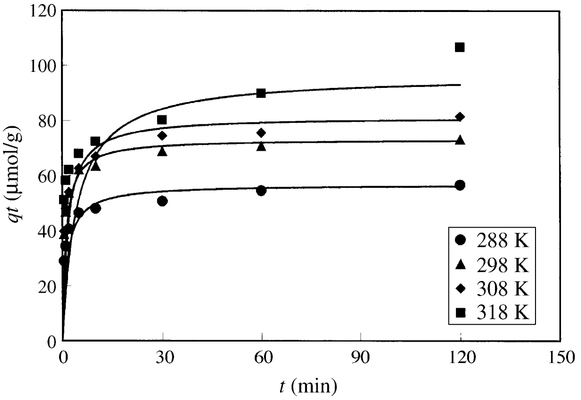

Fig. 4. Plots of adsorbed paraquat amount vs. time at various temperatures (initial concentration = 30 mg/L (i.e., 116.6 μmol/L), adsorbent dosage = 0.5 g/2 L, initial pH 11.0 and agitation speed = 400 rpm; symbols: experimental data, full lines: calculated from Eq. (2) and Table 4).

Table 4
Kinetic parameters for paraquat adsorption onto the regenerated clay at various temperatures[a]

Temperature (K)	k (g/mmol min)	q_e (μmol/g)	Correlation coefficient	C_e (μmol/g)
288	12.3	56.7	0.9993	102.4
298	12.6	73.3	0.9997	98.3
308	7.5	81.4	0.9987	96.3
318	2.3	96.4	0.9859	92.5

[a] Adsorption conditions: initial concentration = 30 mg/L (i.e., 116.6 μmol/L), adsorbent dosage = 0.5 g/2 L, initial pH 11.0, agitation speed = 400 rpm.

4. Conclusions

The use of regenerated clay mineral from spent bleaching earth for the kinetics of paraquat adsorption from aqueous solution has been examined. The following conclusions can be drawn:

1. Initially, the rate of adsorption of paraquat onto the clay adsorbent is rapid. This is then followed by a slower rate and gradually approaches a plateau.
2. The adsorption kinetics can be described by the pseudo-second order model equation.

3. The effect of the initial pH, NaCl concentration and alkali metal ion on the rate of adsorption and the equilibrium adsorption at 25 °C was found to be of considerable significance in the ion exchange process and could be explained by competitive adsorption (in line with those of the similar adsorption systems, e.g., activated bleaching earth-paraquat).
4. The equilibrium adsorption increased with an increase in the temperature, showing that the adsorption system is postulated to be endothermic.
5. The above results suggest that regenerate clay mineral from edible oil industry's waste can be used as a low-cost mineral adsorbent for the removal of cationic pesticides (e.g. paraquat) from an aqueous environment.

Acknowledgement

This research was supported by National Science Council (NSC), Taiwan, under Contracts NSC 90-2815-C-041-002-E.

References

[1] I.H. Lee, S.S. Weng, G.C. Lee, Studies on pesticide residues in water sources: Taiwan area, Taiwan Agric. 27 (1992) 22 (in Chinese).

[2] M. Fernandez, M. Ibanez, Y. Pico, J. Manes, Spatial and temporal trends of paraquat, diquat, and diffenzoquat contamination in water from marsh areas of the Valencian community (Spain), Arch. Environ. Contam. Toxicol. 35 (1998) 377.

[3] L. Ritter, K. Solomon, P. Sibley, K. Hall, P. Keen, G. Mattu, B. Linton, Sources, pathways, and relative risks of contaminants in surface water and groundwater: a perspective prepared for the walkerton inquiry, J. Toxicol. Environ. Health (A) 65 (2002) 1.

[4] S.K. Khan, Pesticides in the Soil Environment, Elsevier, Amsterdam, 1980.

[5] W.C. Lee, M.F. Hsu, T.L. Hu, W.L. Ko, Studies on survey of wastewater-containing phenol and paraquat from the pesticide manufacturing factories (in Chinese), Ind. Pol. Control 20 (1986) 185.

[6] M.Y. Chiang, C.C. Chung, Y.L. Chang, Y.M. Weng, Survey reports on pesticide residues in the effluent discharges of pesticide plants (in Chinese), Ann. Rept. NIEA Taiwan 2 (1994) 157.

[7] R.H. Bromilow, Paraquat and sustainable agriculture, Pest. Manag. Sci. 60 (2004) 340.

[8] C.M. Chen, A.C. Lua, Lung toxicity of paraquat in the rat, J. Toxicol. Environ. Health (A) 59 (2000) 477.

[9] Taiwan Environmental Protection Administration (EPA), Drinking Water Management Act. Available from: http://law.epa.gov.tw/en/laws/water/drinking.html.

[10] Taiwan Council of Agriculture (COA), Food Administration Act. Available from: http://www.coa.gov.tw/coa/eng/law/law02.html.

[11] M.K. Hasnuddin Siddiqui, Bleaching Earth, Pergamon Press, London, 1968.

[12] H.B.W. Patterson, Bleaching practices in Europe, J. Am. Oil Chem. Soc. 53 (1976) 339.

[13] K.S. Low, C.K. Lee, A.M. Wong, Carbonized spent bleaching earth as a sorbent for some organic dyes, J. Environ. Sci. Health A31 (1996) 673.

[14] C.K. Lee, K.S. Low, L.C. Chung, Removal of some organic dyes by hexane-extracted spent bleaching earth, J. Chem. Tech. Biotechnol. 69 (1997) 93.

[15] W.T. Tsai, H.P. Chen, J.M. Yang, Adsorption of paraquat on the physically activated bleaching earth waste from soybean oil processing plant, J. Environ. Sci. Health B37 (2002) 453.

[16] W.T. Tsai, M.F. Hsieh, H.F. Sun, S.F. Chien, H.P. Chen, Adsorption of paraquat onto activated bleaching earth, Bull. Environ. Contam. Toxicol. 69 (2002) 189.

[17] W.T. Tsai, C.W. Lai, K.J. Hsien, Effect of particle size of activated clay on the adsorption of paraquat from aqueous solution, J. Colloid Interface Sci. 263 (2003) 29.

[18] W.T. Tsai, C.W. Lai, K.J. Hsien, The effect of pH and salinity on kinetics of paraquat sorption onto activated clay, Colloid Surf. (A) 224 (2003) 99.

[19] W.T. Tsai, C.W. Lai, K.J. Hsien, Adsorption kinetics of herbicide paraquat from aqueous solution onto activated bleaching earth, Chemosphere 55 (2004) 829.

[20] N.K. Hamadi, S. Swaminathan, X.D. Chen, Adsorption of paraquat dichloride from aqueous solution by activated carbon derived from used tires, J. Hazard. Mater. B112 (2004) 133.

[21] W.T. Tsai, H.P. Chen, M.F. Hsieh, H.F. Sun, S.F. Chien, Regeneration of spent bleaching earth by pyrolysis in a rotary furnace, J. Anal. Appl. Pyrol. 63 (2001) 157.

[22] Association of Official Analytical Chemists (AOAC), Official Methods of Analysis of AOAC International, 17th ed., AOAC International, Arlington, Virginia, 2000.

[23] Y.S. Ho, C.C. Chiang, Sorption studies of acid dye by mixed sorbents, Adsorption 7 (2001) 139.

[24] Y.S. Ho, C.C. Chiang, Y.C. Hsu, Sorption kinetics for dye removal from aqueous solution using activated clay, Sep. Sci. Technol. 36 (2001) 2473.

[25] F.C. Wu, R.L. Tseng, R.S. Juang, Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan, Water Res. 35 (2001) 613.

[26] W.J. Deutsch, Groundwater Geochemistry: Fundamentals and Applications to Contamination, CRC Press, Boca Raton, Florida, 1997.

[27] K. Draoui, R. Denoyel, M. Chgoura, J. Rouquerol, Adsorption of paraquat on minerals: a thermodynamic study, J. Therm. Anal. Cal. 58 (1999) 597.

[28] A. de Keizer, Adsorption of paraquat ions on clay minerals: electrophoresis of clay particles, Progr. Colloid Polym. Sci. 83 (1990) 118.

[29] G. Rytwo, S. Nir, L. Margulies, Adsorption and interactions of diquat and paraquat with montmorillonite, Soil Sci. Soc. Am. J. 60 (1996) 601.

[30] T. Undabeytia, S. Nir, T. Polubesova, G. Rytwo, E. Morillo, C. Maqueda, Adsorption–desorption of chlorimeform on montmorillonite: effect of clay aggregation and competitive adsorption with cadmium, Environ. Sci. Technol. 33 (1999) 864.

[31] T. Nakamura, N. Kawasaki, H. Ogawa, S. Tanada, M. Kogirima, M. Imaki, Adsorption removal of paraquat and diquat onto activated carbon at different adsorption temperature, Toxicol. Environ. Chem. 70 (1999) 275.

[32] W.T. Tsai, Y.M. Chang, C.W. Lai, C.C. Lo, Adsorption of basic dyes in aqueous solution by clay adsorbent from regenerated bleaching earth, Appl. Clay Sci. 29 (2005) 149.