Adsorption of Chromium(VI) and Nickel(II) Ions on Acid- and Heat-Activated Deoiled Spent Bleaching Clay

C.E. Seng*, C.G. Lee, and K.Y. Liew

School of Chemical Sciences, Universiti Sains Malaysia, 11800, Penang, Malaysia

ABSTRACT: De-oiled spent bleaching clay was activated either by acid treatment followed by heat activation or by heat activation alone at temperatures between 200 and 800°C. The surface area of the heat-activated clay attained a maximal value of ~120 $m^2 g^{-1}$ at temperatures between 400 and 500°C while the acid-heat-treated clay attained maximal surface area of ~140 $m^2 g^{-1}$. The adsorption capacities of chromium [Cr(VI)] for both series studied increased as the activation temperature increased until 300°C and decreased again at higher temperatures. At lower pH, more than 95 % of the Cr(VI) was absorbed in a solution with initial concentration of 1 mg L^{-1} per gram of adsorbent activated at 300°C. The adsorption patterns followed Freundlich's isotherms. Two maximal values of adsorption capacities of nickel [Ni(II)] were observed at activation temperatures of 200 and 500°C for acid-treated samples, whereas these were at 200 and 700°C for the nonacid-treated samples. The amount of Ni(II) adsorbed increased with the pH of the solution for all samples studied. The maximal adsorption capacities of the adsorbents in solution containing initial Ni(II) concentration of 5 mg L^{-1} per 0.5 g of adsorbent and at pH 6 were found to be 44 and 42%, respectively, for the acid-treated sample activated at 500°C and for the nonacid-treated sample activated at 700°C. They all obeyed both the Langmuir's and Freundlich's isotherms.

Paper no. J9750 in *JAOCS 78,* 831–835 (August 2001).

KEY WORDS: Adsorption, chromium(VI), nickel(II), spent bleaching clay.

The issue of heavy metals such as chromium [Cr(VI)] and nickel [Ni(II)] in aquatic systems is of considerable interest because of their cumulative toxicity to aquatic organisms. These problems are increasingly felt by nations as the number of industrial establishments increases rapidly. Industries as well as agricultural and municipal sectors are directly affected by any discharge of these heavy metals into their water sources. A number of methods can be used to remove the heavy metals. Among these are chemical precipitation, membrane filtration, ion exchange, and adsorption (1). In industries, commercial activated carbon, with relatively large surface area and good adsorption capability, is used in the treatment system employing simultaneous adsorption and biodegradation processes. However, because of its high cost, researchers are looking for other viable adsorbents as substitutes. A number of researchers have recently investigated the use of solid industrial and agro-based wastes as adsorbents for heavy metals (2–5).

Spent bleaching clay contains about 30–40% oil by weight and constitutes a major loss of oil for the oil processing industries. Also the use and disposal of the spent bleaching clay are becoming a potential problem of concern in the producing countries because of the rapid growth of the industry and the concomitant rapid increase in the generation of the waste materials. Currently, oil-laden spent bleaching clays are mainly disposed of in landfills (6–9) or in waste dumping ground as the spent clays are considered nontoxic. This method of disposal causes environmental concern because of their pyrolytic nature and also the possibility of the leaching of the oil into the surrounding water resources. While efforts to reduce the loss of oil and to minimize clay dosage in the refining process continue, the possibility of recycling the clay has been studied and reviewed (10,11).

Various alcohols and hydrocarbons have been used as solvents to extract the residual oil in spent bleaching clay from palm oil refining (12). It was found that the oil content and minor components in the spent clay were >40% by weight. The efficiencies of extraction by the polar alcohols, except for methanol, were higher but with a slower initial rate than the nonpolar hydrocarbons. The free fatty acids contents, the Totox values, and the color of the alcohol-extracted oil were also higher than those by the hydrocarbons resulting in poorer quality oils.

The objective of this research therefore was to evaluate the efficacy of the removal of heavy metals ions, Cr(VI) and Ni(II) ions as examples, by using reactivated spent bleaching clay.

EXPERIMENTAL PROCEDURES

Fresh spent bleaching clays were collected from a palm oil refiner (Golden Agriculture Pte. Ltd., Penang, Malaysia). The clay used in this investigation was mainly composed of montmorillonite [$(OH)_4Al_4Si_8O_{20}\cdot nH_2O$]. The spent clay contained about 37.2% oil by weight of clay and 16.0% moisture. The spent bleaching clay (~30 g) was deoiled by a modified Soxhlet extraction using hexane (4 h) followed by methanol

---

*To whom correspondence should be addressed. E-mail: ceseng@usm.my

Copyright © 2001 by AOCS Press

(6 h). Deoiled samples were dried at 120°C for 24 h and stored in a stoppered bottle. The deoiled clays were divided into two portions. One portion with 20–30 g of dry deoiled clay was treated with 500 mL of 20% sulfuric acid with stirring for 5 h. The acid-activated sample was washed with water until the washings were of constant pH; then they were rinsed with distilled water. Both acid-treated and nonacid-treated samples were heat-activated for 8 h at temperatures between 200 and 800°C. These samples are designated heat-treated and acid-heat-treated samples.

Nitrogen adsorption experiments were carried out at 77 K by a volumetric method with an automated accelerated surface area and porosimetry system (Model ASAP 2000; Micromeritics Instrument Corporation, Norcross, GA). Heat-treated and acid-heat-treated samples (0.2–0.3 g) were degassed at 125°C for 3 h prior to the adsorption experiments.

Cr(VI) and Ni(II) ion aqueous solutions were prepared from potassium dichromate and nickel sulfate, respectively. Analytical-grade sulfuric acid and hydrochloric acid were used to adjust the pH.

Batch adsorption experiments were carried out in 120-mL capacity plastic bottles with cap by mixing a known amount of adsorbent with Cr(VI) or Ni(II) ion solution of desired concentration and pH and shaking well for a specific period of time at 30°C. Then they were filtered, and the concentration of the metal ion in the filtrate was determined by using a flame-absorption spectrophotometer (Model 3100; PerkinElmer, Norwalk, CT). Preliminary experiments had shown that all the adsorbents had already achieved a maximal uptake of the metal ions at the end of 4 to 6 h, and beyond this time the increase in adsorption was negligible. However, the mixtures were shaken for 12 h to ensure determination of maximal adsorption capacities of some of the adsorbents. The metal adsorption studies were also carried out using unused bleaching clay (UC) as reference sample and a commercial-grade activated carbon (AC) for comparison. In separate experiments, blanks, consisting of metal ion solutions for each metal with no adsorbent, were treated like the sample to find out if there is adsorption of the metal ion by the plastic bottle or filter paper. The adsorption of metal ion was found to be negligible.

RESULTS AND DISCUSSION

Reactivated deoiled spent bleaching clay. Deoiled spent bleaching clay was reactivated either by acid treatment followed by heat activation or by heat activation alone at temperatures between 200 and 800°C. The cation exchange capacity for deoiled clay and the surface areas of heat-activated clay against activation temperatures are shown in Figure 1. The surface area increased with the activation temperatures until 400°C and decreased after 600°C. The surface area of the spent clay increased initially as the adsorbed water and residual oil were driven off as treatment temperature increased until 400°C. Higher treatment temperature after 600°C led to a collapse of the structure (11). The surface areas of the heat-activated clay attained a maximal value of about 120 m^2 g^{-1} at temperatures between 400 and 500°C, while acid-treated clay attained a slightly higher value of 140 m^2 g^{-1} at a similar range of temperature (data not shown).

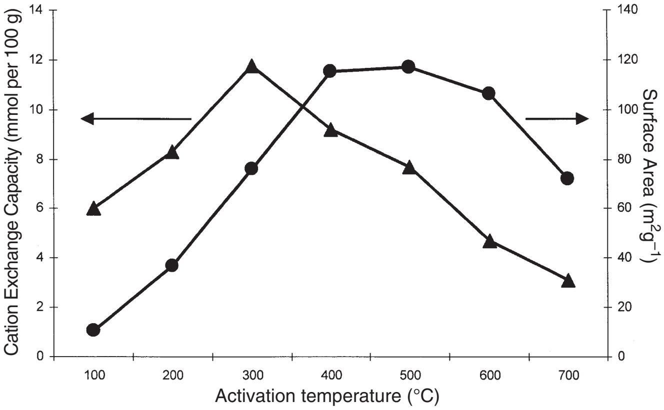

FIG. 1. Cation exchange capacity and the surface area of heat-activated deoiled clay as a function of activation temperature.

The cation exchange capacity reached a maximal value of 11.8 mmol per 100 g of sample after activation at 300°C and decreased gradually to 3.1 mmol per 100 g sample when activated at 700°C. However, the maximal surface area at 400°C did not correspond to the optimal condition for cation exchange capacity. The cation exchange capacity is thus not a linear function of the specific surface area of the clay, presumably because some of the cation exchange sites, such as the Brönsted acids, were removed because of dehydroxylation and decrease in surface area at higher temperature.

Adsorption of Cr(VI) ions. Adsorption capacities increased as the activation temperatures increased until 300°C for the acid-heat-treated sample (S300A) (Fig. 2). The adsorption capacities decreased after 300°C, and there was less than 20% removal of Cr(VI) from 1 ppm initial concentration with 1 g L^{-1} of adsorbent after activation at 600°C. On the other hand, the heat-treated sample (S200) showed maximal adsorption capacity when activated at 200°C (Fig. 3). The adsorption capacities decreased after 200°C, and less than 10% removal of Cr(VI) could be achieved when activated at 500°C.

The adsorption of the Cr(VI) ions on solid surfaces is also

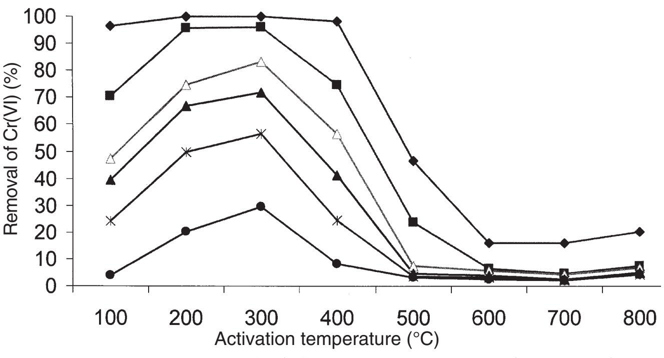

FIG. 2. Percentage removal of chromium [Cr(VI)] as a function of activation temperature for acid-treated samples. Conditions: Cr(VI) concentration, 1 ppm; adsorbent dosage, 1 g L^{-1}; temperature, 30°C; ◆ pH 2, ■ pH 3, △ pH 4, ▲ pH 8, ✳ pH 10, ● pH 11.

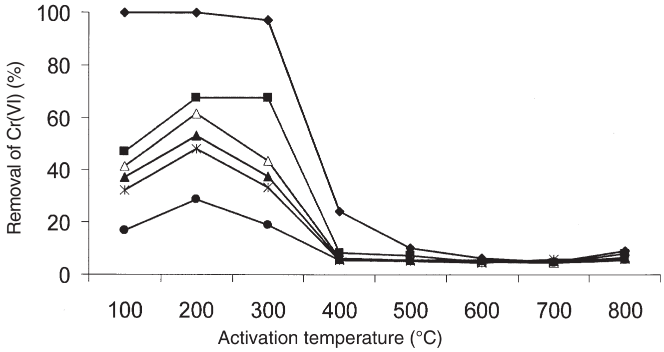

FIG. 3. Percentage removal of Cr(VI) as a function of activation temperature for heat-treated samples. Conditions: Cr(VI) concentration, 1 ppm; adsorbent dosage, 1 g L^{-1}; temperature, 30°C; ◆ pH 2, ■ pH 3, △ pH 6, ▲ pH 9, ✳ pH 10, ● pH 11.

pH-dependent. At pH 2, 100% removal of Cr(VI) was observed for acid-heat-treated samples at activation temperatures of 200 (S200A) and 300°C (S300A) (Fig. 2), whereas this was observed for the heat-treated samples at 100 and 200°C (Fig. 3). The greater adsorption capacity was observed at lower pH for both samples. Higher adsorption capacities of Cr(VI) at all the pH values studied were found for the acid-heat-treated and the heat-treated samples at 300 and 200°C, respectively. The highly acidic conditions facilitate the adsorption of Cr(VI) ion because it is present in solution as CrO_4^{2-} or $Cr_2O_7^{2-}$. Maximal adsorption of Cr(VI) in acidic aqueous solutions has been reported by several researchers (4,13).

It is noted from Figures 2 and 3 that acid-heat-treated samples always showed better adsorption capacities than heat-treated samples. Because of the high adsorption capacities at low pH, acid-heat-treated samples provided lower pH and increased the adsorption capacities. This indicated that the active sites for the adsorption of Cr(VI) ion were most probably the acidic sites.

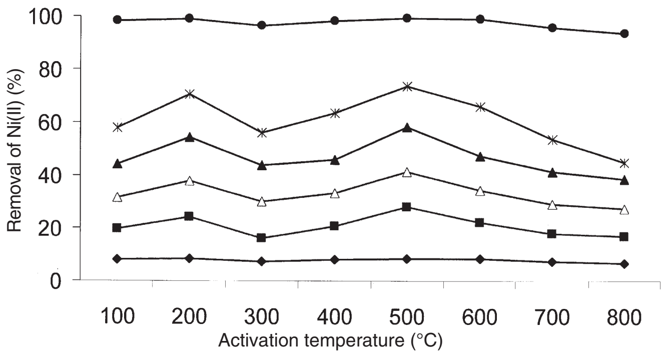

FIG. 4. Percentage removal of nickel [Ni(II)] as a function of activation temperature for acid-treated samples. Conditions: Ni(II) concentration, 5 ppm; adsorbent dosage, 0.5 g L^{-1}; temperature, 30°C; ◆ pH 2, ■ pH 4, △ pH 5, ▲ pH 8, ✳ pH 9, ● pH 11.

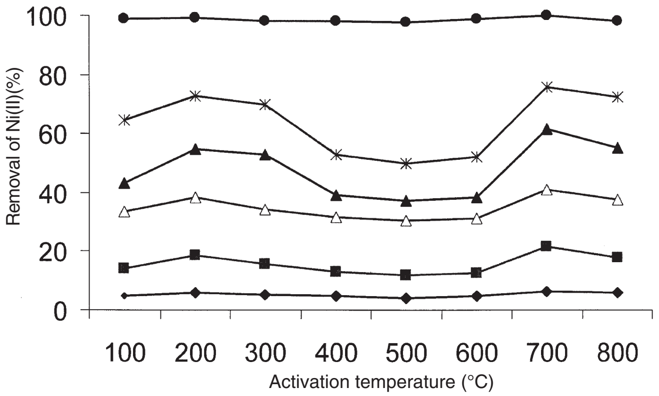

FIG. 5. Percentage removal of Ni(II) as a function of activation temperature for heat-treated samples. Conditions: Ni(II) concentration, 5 ppm; adsorbent dosage, 0.5 g L-1; temperature, 30°C; ◆ pH 2, ■ pH 3, △ pH 5, ▲ pH 8, ✳ pH 9, ● pH 11.

Adsorption of Ni(II) ions. The adsorption of Ni(II) ions at an initial concentration of 5 ppm with 0.5 g L^{-1} adsorbent was studied at 30°C. Two maximal values of adsorption capacities for Ni(II) ion were observed at 200 and 500°C for the acid-heat-treated samples, whereas these were observed at 200 and 700°C for the heat-treated samples. Both showed better adsorption capacities at 200°C. The adsorption capacities for samples activated at other temperatures did not vary substantially.

Figures 4 and 5 showed that the adsorption of Ni(II) ion increased with increasing pH. At pH 10 and 11, more than 90% of the Ni(II) ion was adsorbed. At high pH, precipitation of the insoluble hydroxides occurred, removing Ni(II) ion from solution. It has been reported that hydrolysis and precipitation occur at pH 6 and pH 8 (14).

The maximal adsorption capacity for acid-heat-treated samples and heat-treated samples was observed at activation temperatures of 500 and 700°C, respectively. At pH 11, 99.4 and 100% of Ni(II) ions were removed for the acid-heat-treated samples and heat-treated samples, respectively, at their optimal activation temperatures. This showed that the heat-treated samples had higher adsorption capabilities as compared to the acid-heat-treated samples at their optimal activation temperatures, as a result of the presence of inherent acidity for acid-heat-treated samples, which would reduce the precipitation process. Unlike Cr(VI) ion, there was only slight adsorption of Ni(II) ion at low pH values.

Adsorption isotherms. Freundlich's isotherm was evaluated by plotting Equation 1,

$$\log Q_e = \log K_F + 1/n \log C_e \qquad [1]$$

where Q_e is the quantity adsorbed per gram of adsorbent, C_e is the equilibrium adsorbate concentration, K_F is the adsorption capacity constant, and n is a measure of the affinity or interaction energy between the adsorbate and the adsorbent. Figures 6 and 7 show the plot of log Q_e against log C_e for the adsorption of Cr(VI) ions for samples, UC and AC. The linear plots show that Cr(VI) adsorption followed Freundlich's isotherms, with the constants $1/n$ and K_F shown in Table 1.

In Table 1, the value of K_F for pH 2 is higher than that for pH 3, and sample S300A in turn showed a higher value of K_F than that for S200A. The results confirmed the previous finding on pH and activation temperature on adsorption of Cr(VI) ions. The data for the adsorption of Cr(VI) on the various

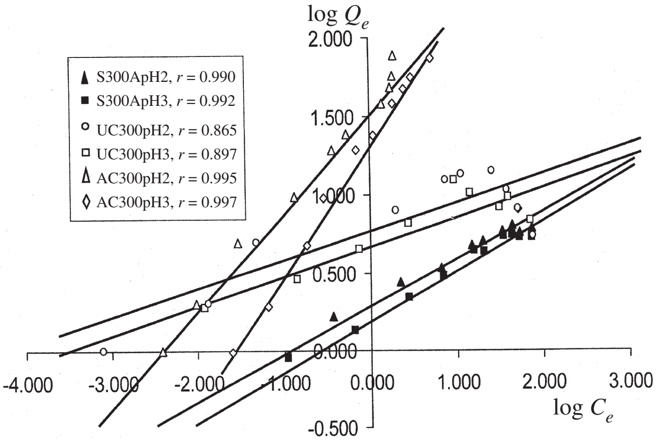

FIG. 6. Freundlich's isotherms for samples S300A, unused bleaching clay (UC)300, and activated carbon (AC)300 at pH 2 and pH 3 for adsorption of Cr(VI). See Equation 1. Conditions: adsorbent dosage, 1 g L^{-1}; temperature, 30°C

adsorbents indicate that commercial-grade AC adsorption was the best among the three types of adsorbents studied.

When log Q_e was plotted against log Q_e for the adsorption of Ni(II) ions at pH 9 for S500A and S700 samples, UC and AC (Fig. 8), reasonably good straight lines were obtained for all the samples. The parameters for the Freundlich equation for various adsorbents are presented in Table 2. It is observed that adsorption capabilities of both samples of spent bleaching clay, S500A and S700, were almost the same.

The constant n in the Freundlich equation indicates affinity or interaction energy between the adsorbent and the adsorbate. The value of $1/n$ also indicates the preference of the adsorption process. If $1/n < 1$, the rate of change of concentration of adsorbed substance is smaller than the rate of change in solution. Such an adsorption is favorable (15,16). All the values of $1/n$ in Table 1 are within the range of 0.1 to 0.9, indicating that good adsorption mechanisms were observed for all the above samples studied.

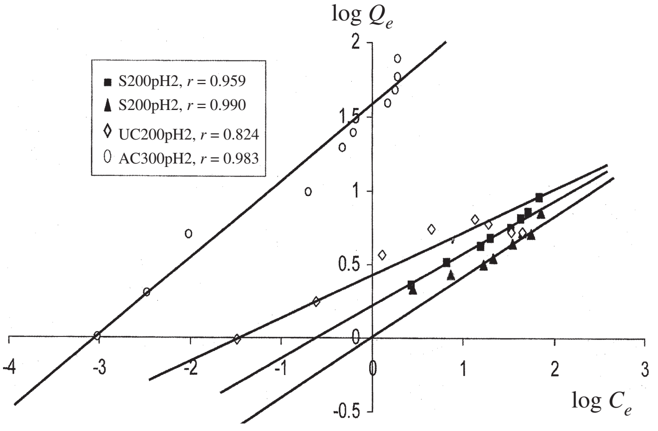

FIG. 7. Freundlich's isotherms for samples S200A, S200, UC200 and AC200 at pH 2 for adsorption of Cr(VI). Conditions: adsorbent dosage, 1 g L^{-1}; temperature, 30°C. See Figure 6 for abbreviations.

TABLE 1
Freundlich Equation Constants for Samples S300A, S200A, S200, UC200, UC300, AC200 and AC300 on Adsorption of Cr(VI) Ions at pH 2 and pH 3[a]

Sample	Constants	pH 2	*r*	pH 3	*r*
S300A	1/*n*	0.263	0.990	0.305	0.992
	K_F	2.203		1.671	
S200A	1/*n*	0.393	0.990		
	K_F	1.495			
S200	1/*n*	0.346	0.959		
	K_F	1.349			
UC200	1/*n*	0.193	0.824		
	K_F	2.630			
UC300	1/*n*	0.190	0.865	0.186	0.897
	K_F	5.585		4.742	
AC200	1/*n*	0.505	0.983		
	K_F	35.48			
AC300	1/*n*	0.636	0.995	0.837	0.997
	K_F	38.02		21.88	

[a] UC, unused bleaching clay; AC, activated carbon; *n*, a measure of the affinity or interaction energy between the absorbate and the absorbed; K_F, adsorption capacity constant; *r*, correlation coefficient.

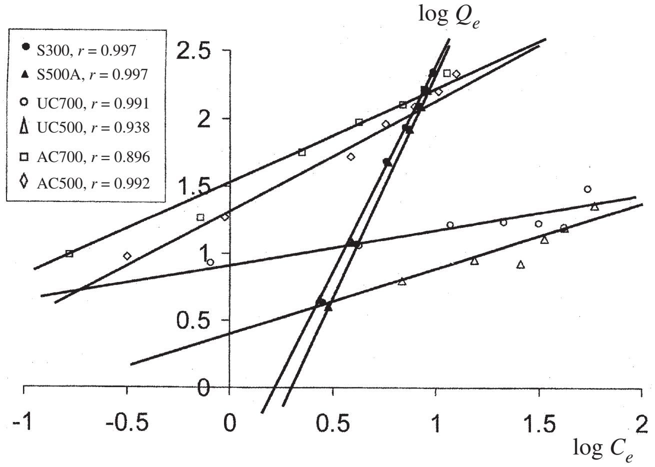

FIG. 8. Freundlich's isotherms for samples S700, S500A, UC700, UC500, AC700, and AC500 at pH 9 for adsorption of Ni(II). Conditions: adsorbent dosage, 0.5 g L^{-1}; temperature, 30°C. See Figure 6 for abbreviations.

TABLE 2
Freundlich's Constants for Samples S500A, S700, UC500, UC700, AC500, and AC700 on Adsorption of Ni(II) Ions at pH 9[a]

Sample	Constants	pH 9	*r*
S500A	1/*n*	3.31	0.997
	K_F	0.117	
S700	1/*n*	3.30	0.997
	K_F	0.121	
UC500	1/*n*	0.480	0.938
	K_F	2.535	
UC700	1/*n*	0.242	0.896
	K_F	8.381	
AC500	1/*n*	0.847	0.992
	K_F	21.38	
AC700	1/*n*	0.755	0.991
	K_F	30.20	

[a] See Table 1 for abbreviations.

REFERENCES

1. Sandstrom, D.W., and H.E. Klei, *Waste Water Treatment*, Prentice-Hall, Englewood Cliffs, NJ, 1979, pp. 28–37.
2. Cimino, G., A. Passerini, and G. Toscano, Removal of Toxic Cations and Cr(VI) from Aqueous Solution by Hazelnut Shell, *Water Res. 34*:2955–2962 (2000).
3. Candela, M.P., J.M.M. Martinez, and R.T. Macia, Chromium(VI) Removal with Activated Carbons, *Ibid. 29*: 2174–2180 (1995).
4. Bansal, T.K., and H.R. Sharma, Chromium Removal by Adsorption on Rich Husk Ash, *Indian J. Environ. Protection 12*:198–201 (1992).
5. Periasamy, K., and C. Namasivayam, Removal of Ni(II) from Aqueous Solution and Nickel Plating Industry Wastewater Using an Agricultural Waste: Peanut Hulls, *Waste Manage. 15*: 63–68 (1995).
6. Wong, H.H., Quality of By-Products from Chemical and Physical Refining of Palm Oil and Other Oils, *J. Am. Oil Chem. Soc. 60*:316–321 (1983).
7. Svensson, C., Use or Disposal of By-Products and Spent Material from the Vegetable Oil Processing Industry in Europe, *Ibid. 53*:443–445 (1976).
8. Waston, K.S., and M. Hoefer, Use or Disposal of By-Product and Spent Material from the Vegetable Oil Processing Industry in the U.S., *Ibid. 53*:437–443 (1976).
9. Ong, J.T.L., Oil Recovery from Spent Bleaching Earth and Disposal of the Extracted Material, *Ibid. 60*:314–315 (1983).
10. Kalam, A., and J.B. Jashi, Regeneration of Spent Earth in Aqueous Medium, *Ibid. 65*:1917–1921 (1988).
11. Ng, K.F., N.K. Nair, K.Y. Liew, and M.N. Ahmad, Surface and Pore Structure of Deoiled Acid- and Heat-Treated Spent Bleaching Clay, *Ibid. 74*:963–970 (1997).
12. Lee, C.G., C.E. Seng, and K.Y. Liew, Solvent Efficiency for Oil Extraction from Spent Bleaching Clay, *Ibid. 77*:1219–1222 (2000).
13. Chung, Y.S., K.W. Lee, Y.S. Yoon, S.H. Kwon, and K.S. Lim, The Adsorption Behaviours of Heavy Metals Ions on the Sawdusts, *Bull. Korean Chem. Soc. 13*:212–214 (1992).
14. Coupal, B., and J.M. Lalancette, The Treatment of Waste Waters with Peat Moss, *Water Res. 10*:1071–1076 (1976).
15. Hassler, J.W., *Purification with Activated Carbon*, Chemical Publishing Co., New York, 1974, pp. 53–54.
16. Mckay, G., M.S. Otterburn, and A.G. Sweeney, The Removal of Colour from Effluents Using Various Adsorbent. III: Silica-Rate Process, *Water Res. 14*:15–27 (1980).

[Received August 31, 2000; accepted April 28, 2001]