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Adsorptive Removal of Cobalt from Aqueous Solutions by Utilizing Industrial Waste and its Cement Fixation

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Abstract: In the present study, the adsorption potential of battery industry waste as adsorbent has been investigated for the removal of cobalt from aqueous solutions. The results have shown that the prepared adsorbent adsorbs cobalt to a sufficient extent (35 mg/g). The adsorption of cobalt has been studied on this battery industry waste as a function of contact time, concentration, and temperature by the batch method. The adsorption has been found to be endothermic and the data conform to the Langmuir equation. The analysis of kinetic data indicates that adsorption is a first order process and pore-diffusion controlled.

Further, the metal-laden adsorbent was immobilized into cement for ultimate disposal and no significant leaching was observed from the stabilized products. Thus, the present study clearly reveals that battery industry waste can be fruitfully employed in treating industrial effluents containing toxic metal ions.

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The proposed technology (utilization of industrial wastes for effluent treatment and then ultimate disposal of adsorbents laden with pollutants in cementitious materials by fixation) provides a twofold aim of wastewater treatment and solid waste management.

Keywords: Industrial waste minimization, battery industry waste, adsorbent, cobalt removal, water treatment

INTRODUCTION

The rapid pace of unplanned urbanization, industrialization, population growth, and utilizing every bit of natural resources resulted in deterioration of the environment. Pollution caused through various industrial, agricultural, and domestic activities has reached critical levels causing various kinds of health problems. The risk factors associated with the disposal of toxic industrial wastes is a matter of great concern, especially in developing countries, where lack of knowledge regarding adequate treatment of solid wastes, including industrial wastes makes the situation more difficult. As a result of the development of better analytical systems and better health monitoring technologies, the acceptable minimum concentration of these pollutants is progressively decreasing. This has forced industries to look for cost effective technologies for treating their wastewater before mixing them with good quality of natural water. Various treatment technologies for effluent treatment have been developed to control the water pollution (1). Some of them are coagulation, sedimentation, floatation, filtration, ion exchange, membrane process, adsorption, chemical precipitation, and disinfection.

Among them, the adsorption process is considered better for wastewater treatment as compared to other methods because of convenience, easy operation, and simplicity of design. Further, this process can remove/minimize different types of pollutants and thus, it has a wider applicability in water pollution control (2). Activated carbon has been found to be a versatile adsorbent, which can remove diverse types of pollutants such as metal ions, dyes, phenols, and a number of other organic and inorganic compounds and bio-organisms. However, its use is sometimes restricted due to higher cost if compared to other physical and chemical treatment processes. Attempts have therefore, been made to utilize low cost alternative adsorbents. The aim behind this is to minimize the cost of the adsorbent so that the regeneration can be dispensed with. Utilization of industrial waste materials is of vital concern over the past few years because these wastes represent unused resources and, in many cases, cause serious disposal problems. The aim behind using waste materials as adsorbents is that it will provide a two-fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly, if an efficient low cost adsorbent could be developed, it can treat industrial effluents at a reasonable cost. Thus, a number of industrial wastes (3–12) have been investigated so far with or without treatment as adsorbents for the removal of pollutants from wastewaters. However, these have not been found to be much successful in water pollution control. Therefore, the search for a low-cost adsorbent is still going on. Further, most of these studies did not suggest any environmentally safe disposal method of metal-laden adsorbent generated from the adsorption process.

Compared to other heavy metal ions, little attention has been focused on cobalt removal from water and wastewaters. However, adsorption studies of cobalt are important from the nuclear and hazardous waste management point of view. Only few studies report satisfactory adsorption potential for cobalt onto different adsorbents, for example, *marine green alga* $= 46\ \mathrm{mg/g}$ (13); *IRN77* $= 86\ \mathrm{mg/g}$ (14); *SKN1* $= 69\ \mathrm{mg/g}$ (14); *natural vermiculite* $= 49\ \mathrm{mg/g}$ (15) etc. However, no report is available where the adsorption efficacy of battery industry waste has been investigated for cobalt removal from water. The aim of this study was to determine the efficiency of battery industry waste as adsorbent for the removal of cobalt from aqueous solutions. Equilibrium and kinetic studies were performed to describe the adsorption process. Different models were tested to determine the rates and mechanisms of the adsorption process. The study was further extended to immobilize the metal-laden adsorbent into cement for environmentally safe disposal. Finally, the leachability from the fixed-product (solidified waste) was studied.

EXPERIMENTAL

Reagents and Materials

Solutions were prepared from $Co(NO_3)_2 \cdot 6H_2O$ salt in double distilled water and were diluted further to obtain the lower concentration solutions. Commercial Ordinary Portland cement 43 grade was used for the present studies.

Preparation of Low-Cost Adsorbent using Battery Industry Waste

The battery industry waste was procured from M/S Prakash Metal Industries, Mohkampur, Phase I, Meerut (U.P.). It was first washed with double distilled water and dried at 200°C overnight. Then, it was treated with H_2O_2 to remove the organic impurities. It was then washed with distilled water and heated at 200°C. The activation of this material was done at 450°C in a muffle furnace for one hour in the presence of air. After activation, the ash content was removed by washing with distilled water and dried. Different mesh sizes were obtained after sieving and kept in desiccator for further use.

Apparatus

An atomic Absorption Spectrophotometer (AAS) from Hitachi model No. Z-7000 has been used to determine the concentration of cobalt in aqueous solutions. A hazardous waste filtration system from Millipore model No. YT-30142 HW was used to carry out toxicity characteristic leaching procedure as recommended by United States Environmental Protection Agency (US EPA). A compressive strength testing machine from a central scientific instruments company was used to determine the compressive strength of mortar samples. Scanning electron microscope from LEO 438VP, UK was used for the microstructure visualization of the prepared cement samples.

Methods

Adsorption Studies

The adsorption of cobalt on the battery industry waste was studied at room temperature by employing the batch method. A known volume (10 ml) of metal solutions of varying initial concentrations, taken in 50-ml stoppered glass tubes, was shaken with a fixed dose of adsorbent (0.10 g) for a specified contact time in a thermostated shaking assembly. After equilibrium, the concentration of the adsorbate in the residual solution was determined by AAS. The experiments were repeated three times and the average values are reported. Standard deviations were found to be within ±3.0%. Kinetic studies of adsorption were also carried out at two concentrations of the adsorbate.

Preparation and Curing of Cement Pastes and Mortars

A separate batch adsorption experiment similar to that described above but with a larger volume (1 liter) of metal solution with a larger quantity of battery industry waste (10 g) was conducted to produce the metal-laden adsorbent for the preparation of the solidified specimens. After the equilibration time, the solid was separated from the liquid. The metal-laden adsorbent was then dried in an oven at 100°C overnight. After drying, the metal-laden adsorbent was added in different proportions to cement and sand to produce a cementitious system. Well-mixed mortar pastes were cast in 2.78″ cubic iron molds. The cubes were demolded after 24 hours and were kept dipped in water for curing. These cubes were tested for compressive strength at 3, 7, 28, 60, and 90 days of curing. Four replicates were tested every time and the average value was compared with the values obtained for the blank sample. All the cement pastes and mortars were prepared by following the methods described in IS: 4031-1968 guidelines.

Leaching Studies

An appropriate way to examine the effectiveness of the immobilization of contaminants after the solidification process is to perform the leaching test. These tests are commonly used to determine the leachability under the selected leach testing conditions. This study has been carried out by following the standard method No. 1311 as recommended by United State Environment Protection Agency (USEPA). Crushed solid material was placed in hazardous waste filtration system with zero head space extractor. A known volume of water was added and this assembly has been agitated for 24 hours continuously in the agitator. A filtered extract was collected in a closed vessel and was analyzed for metal concentration by using the Atomic Absorption Spectrophotometer (AAS). The results were compared with those obtained for blank samples to know the actual enhancement in the concentration of the metal in the leachate.

RESULTS AND DISCUSSION

Effect of Contact Time and Concentration

In order to find the equilibrium time for the maximum uptake of cobalt on battery industry waste, the adsorption of cobalt on battery industry waste was studied as a function of contact time and the results are shown in Fig. 1. It is seen from Fig. 1 that the rate of uptake of cobalt is rapid in the beginning and 50% adsorption is completed within 2 hours. Figure 1 also

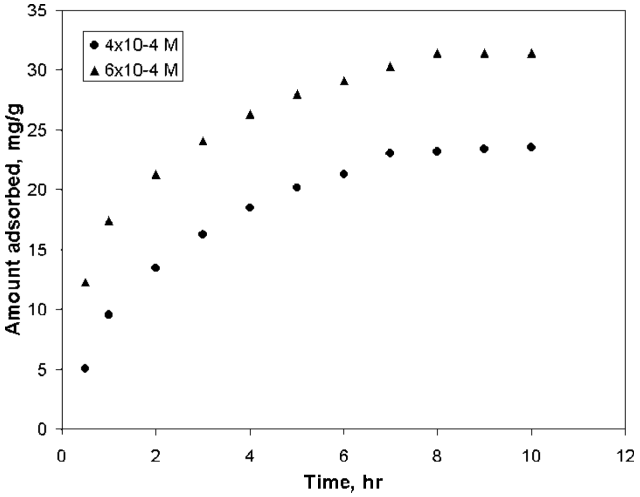

Figure 1. Effect of contact time on uptake of cobalt on battery industry waste at different initial concentrations (particle size: 200–250 mesh; temperature: 25°C).

indicates that the time required for the equilibrium adsorption is 8 hours but the equilibration period of 10 hours was selected for further studies. The effect of concentration on equilibrium time was also investigated at different concentrations and the results are also compiled in Fig. 1. It was found that the time of equilibrium as well as the time required to achieve a definite fraction of equilibrium adsorption is independent of initial concentration. These results indicate that the adsorption process is first order, which is confirmed by Lagergren's plots discussed later under dynamic modelling.

Adsorption Isotherms

In order to determine the efficacy of battery industry waste, the equilibrium adsorption studies were carried out and the adsorption isotherms are shown in Fig. 2. An adsorption capacity of 35 mg/g was observed for cobalt on battery industry waste at 25°C. It is clear from Fig. 2 that initially isotherm rises sharply indicating that plenty of readily accessible sites are available for adsorption. However, after the equilibration period, when the adsorbent is saturated, a plateau is reached indicating that no more sites are available for adsorption.

Effect of Temperature

In order to understand the effect of temperature on the adsorption of cobalt, experiments were also conducted at 45°C and results are compiled in Fig. 2.

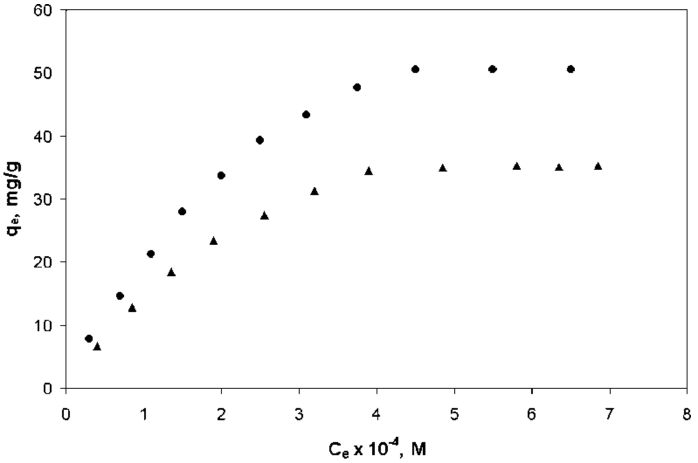

Figure 2. Adsorption isotherms of cobalt on battery industry waste (▲: 25°C; •: 45°C).

A comparison of adsorption isotherms at 25 and 45°C shows that adsorption increases with increase in temperature, indicating that the process is endothermic.

The adsorption data was further analyzed and found to conform best to following Langmuir equation with good correlation coefficients varying from 0.9991 to 0.9995

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \tag{1}$$

where "q_e" is amount adsorbed at equilibrium concentration "C_e", "q_m" the Langmuir constant representing maximum monolayer adsorption capacity, and "b" the Langmuir constant related to energy of adsorption. The plot of $1/q_e$ as a function of $1/C_e$ for the adsorption of cobalt are drawn in Fig. 3. The values of the monolayer adsorption capacity (q_m) and equilibrium constant (b) have been evaluated from the intercept and slope of these plots and given in Table 1.

The influence of the adsorption isotherm shape has been discussed (16) to know whether the adsorption is favorable in terms of "R_L", a dimensionless constant referred to as a separation factor or equilibrium parameter. "R_L" is calculated using the following equation:

$$R_L = \frac{1}{1 + bC_0} \tag{2}$$

The values of "R_L" calculated as per the above equation are incorporated in Table 1. As the "R_L" values lie between 0 and 1, adsorption is favorable towards the contaminant under concern.

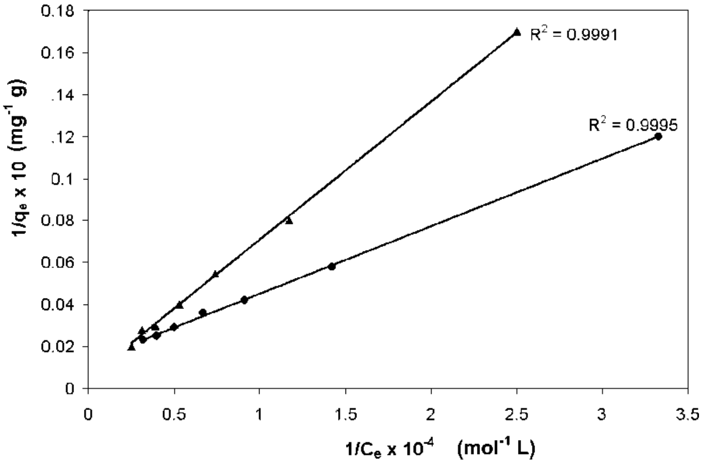

Figure 3. Langmuir adsorption isotherms of cobalt adsorption on battery industry waste at different temperatures (▲: 25°C; ●: 45°C).

Table 1. Langmuir constants and separation factor for the adsorption of cobalt on battery industry waste at different temperatures

Temperature (°C)	q_m (mg/g)	b (L/mol)	R_L
25	48.7	3.4×10^3	0.39
45	67.4	4.0×10^3	0.34

The free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated using following equations:

$$\Delta G^0 = -R\ T \ln(b) \tag{3}$$

$$\ln(b_2/b_1) = -\frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{5}$$

in order to know the nature of the adsorption process and the results are summarized in Table 2. Positive ΔH^0 value indicates that the process in endothermic in nature whereas negative ΔG^0 value indicates a spontaneous process. Positive ΔS^0 value indicates the affinity of the adsorbent for cobalt.

Dynamic Modelling

The kinetics of sorption is one of the important characteristics in defining the efficiency of sorption. Various kinetic models have been proposed by different researchers, where the adsorption has been treated as first order (3, 17), pseudo first order (18, 19), and a pseudo second order process (20). Different systems conform to different models. The Lagergren's rate equation (21) is the one most widely used (3, 17, 22) for the sorption of a solute from a liquid solution. Thus this first order equation

$$\log\ (q_e - q) = \log q_e - \frac{k_{ads}}{2.303}t \tag{6}$$

Table 2. Thermodynamic parameters for the adsorption of cobalt on battery industry waste at different temperatures

Temperature (°C)	$-\Delta G^0$ (kJ/mol)	ΔS^0 (J/mol · K)	ΔH^0 (kJ/mol)
25	19.7	89.8	6.5
45	20.4	91.2	

where "q_e" and "q" are the amount of cobalt adsorbed at equilibrium and at time t, in mg/g respectively, and k_{ads} the first order rate constant, was applied to the present studies of adsorption. As such, the values of log ($q_e - q$) were calculated from the kinetic data of Fig. 1 and plotted against time in Fig. 4. The plots are found to be linear with good correlation coefficients (0.9994) indicating that Lagergren's equation is applicable to the cobalt adsorption on battery industry waste and the adsorption is first order process.

The kinetic data was further used to learn about the slow step occurring in the present adsorption system. The applicability of following Bangham's equation (23)

$$\log\log\left(\frac{C'_0}{C'_0 - q'\,m'}\right) = \log\left(\frac{k_o\,m'}{2.303\,V}\right) + \alpha \log t \tag{7}$$

where C'_o is the initial concentration of the adsorbate in solution (mmol/l), V the volume of the solution (ml), m′ the weight of adsorbent used per liter of solution (g/l), q′ (mmol/g) the amount of adsorbate retained at time t and $\alpha(<1)$ and k_o constants, to present cobalt adsorption studies were used. As such $\log\log[C_o'/(C_o' - q'\ m')]$ was plotted against log t in Fig. 5. The linearity of these plots with good correlation coefficients (0.9997) confirms the applicability of Bangham's equation and indicates that the diffusion into pores of the adsorbent controls the adsorption process.

Compressive Strength of Solidified Products

The compressive strength values of the blank sample as well as of the samples containing 1–20% metal-laden adsorbent are presented in Table 3. The results

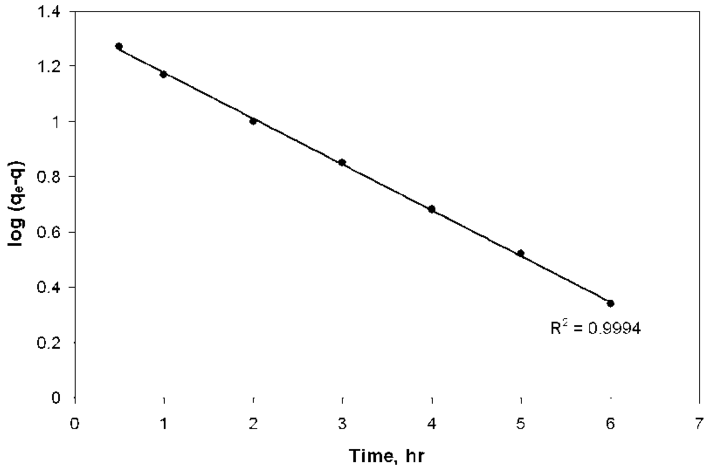

Figure 4. Lagergren's plot for cobalt adsorption on battery industry waste.

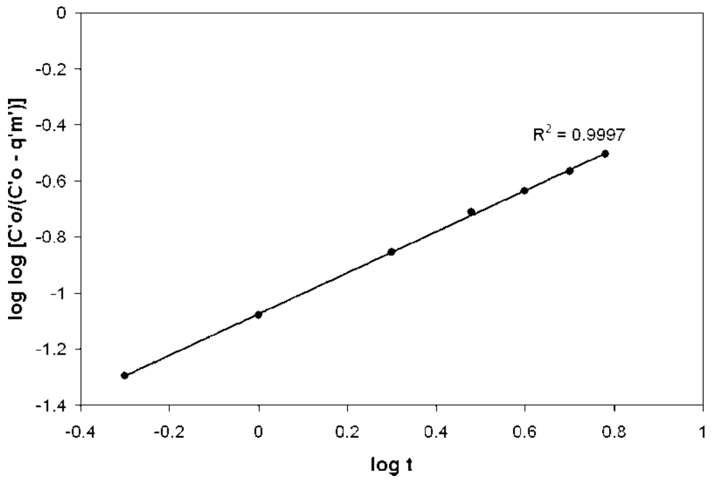

Figure 5. Bangham's plot for cobalt adsorption on battery industry waste.

of the compressive strength on 3, 7, 28, 60, and 90 days of curing are reported here. According to the IS: 8112-1989 for 43 grade Ordinary Portland cement, the compressive strength of cement should be at least 230 kg/cm^2, 330 kg/cm^2 and 430 kg/cm^2 at 3, 7, and 28 days of curing. Great care was taken to reduce the variability associated with batch preparation steps and reagent addition to avoid any substantial variability within a specific batch. It is clear from Table 3 that there is little effect in compressive strength for the samples containing 1–20% metal-laden adsorbent in comparison with controls. The preliminary results of leaching studies indicate that metal ions did not leach out in higher concentrations from the solidified concrete blocks over extended period of time. However, detailed investigations regarding leaching studies of metal ions from cement stabilized battery waste is under progress.

Table 3. Compressive strength of battery industry waste fixed by cement

	Compressive Strength (kg/cm^2) (Number of days)				
Matrix	3	7	28	60	90
Cement + 1.0% Co-laden B.I.W.	312.0	428.0	472.0	555.0	565.0
Cement + 5.0% Co-laden B.I.W.	315.0	422.0	475.0	552.0	561.0
Cement + 10.0% Co-laden B.I.W.	310.0	420.0	470.0	548.5	555.0
Cement + 20.0% Co-laden B.I.W.	305.0	426.0	472.0	552.0	563.0

B.A.I. = Battery Industry Waste.

CONCLUSIONS

The present studies clearly reveal that battery industry waste can be fruitfully employed in treating industrial effluents containing toxic metal ions. The proposed technology (utilization of industrial wastes for effluent treatment and ultimate disposal of adsorbents laden with pollutants in cementitious materials by fixation) provides a twofold aim of wastewater treatment and solid waste management.

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REFERENCES

1. Pontius, F.W. (1990) *Water Quality and Treatments*, 4th Edn; McGraw-Hill, Inc: New York.
2. Faust, S.D. and Aly, O.M. (1987) *Adsorption Process for Water Treatments*; Butterworths Publishers: Stonehams.
3. Panday, K.K., Prasad, G., and Singh, V.N. (1985) Copper(II) removal from aqueous solutions by fly ash. *Water Res.*, 19 (7): 869–873.
4. Sekaran, G., Shanmugasundaram, K.A., Mariappan, M., and Raghvan, K.V. (1995) Utilisation of a solid waste generated in leather industry for removal of dye in aqueous solution. *Ind. J. Chem. Technol.*, 2: 311–316.
5. Lee, C.K., Low, K.S., and Chow, S.K. (1996) Chrome sludge as an adsorbent for colour removal. *Environ. Technol.*, 17 (9): 1023–1028.
6. Çengeloğlu, Y., Kir, E., and Ersöz, M. (2002) Removal of fluoride from aqueous solution by using red mud. *Sep. Purif. Technol.*, 28 (1): 81–86.
7. Calce, N., Nardi, E., Petronio, B.M., and Pietroletti, M. (2002) Adsorption of phenols by papermill sludges. *Environ. Pollut.*, 118 (3): 315–319.
8. Yamada, H., Kayama, M., Saito, K., and Hara, M. (1986) A fundamental research on phosphate removal using slag. *Water Res.*, 20 (5): 547–557.
9. Dimitrova, S.V. (1996) Metal sorption on blast-furnace slag. *Water Res.*, 30 (1): 228–232.
10. López, F.A., Perez, C., Sainz, E., and Alonso, M. (1995) Adsorption of Pb^{2+} on blast furnace sludge. *J. Chemical Technol. Biotechnol.*, 62 (2): 200–206.
11. Jallan, G. and Pandey, G.S. (1992) Blast furnace gas cleaning sludge as adsorbent of some toxic ions. *Res. Ind.*, 37: 143–145.
12. López-Delgado, A., Pérez, C., and López, F.A. (1998) Sorption of heavy metals on blast furnace sludge. *Water Res.*, 32 (4): 989–996.
13. Vijayaraghavan, K., Jegan, J., Palanivelu, K., and Velan, M. (2005) Biosorption of copper, cobalt and nickel by marine green alga ulva reticulata in a packed column. *Chemosphere*, 60 (3): 419–426.

14. Rengaraj, S. and Moon, S.H. (2002) Kinetics of adsorption of Co(II) removal from water and wastewater by ion exchange resins. *Water Res.*, 36 (7): 1783–1793.
15. de Fonseca, M.G., de Oliveira, M.M., Arakaki, L.N.H., Espinola, J.G.P., and Airoldi, C. (2005) Natural vermiculite as an exchanger support for heavy cations in aqueous solutions. *J. Colloid Interface Sci.*, 285 (1): 50–55.
16. Weber, T.W. and Chakravorti, R.K. (1974) Pore and solid diffusion models for fixed bed adsorbers. *J. Am. Inst. Chem. Engg.*, 20: 228–238.
17. Haribabu, E., Upadhya, Y.D., and Upadhyay, S.N. (1993) Removal of phenols from effluents by fly ash. *Int. J. Environ. Stud.*, 43: 169–176.
18. Tutem, E., Apak, R., and Unal, C.F. (1998) Adsorptive removal of chlorophenols from water by bituminous shale. *Water Res.*, 32 (8): 2315–2324.
19. Ho, Y.S. and McKay, G. (1999) The sorption of lead(II) ions on peat. *Water Res.*, 33 (2): 578–584.
20. Ho, Y.S., Ng, J.C.Y., and McKay, G. (2001) Removal of lead(II) from effluents by sorption on peat using second-order kinetics. *Separ. Sci. Technol.*, 36 (2): 241–261.
21. Lagergren, S. (1898) About the theory of so-called adsorption of soluble substances. *K. Svenska Vetenskapsad Handl.*, 24: 1–39.
22. Periasamy, K. and Namasivayam, C. (1984) Process development for removal and recovery of cadmium from wastewater by a low-cost adsorbent: adsorption rates and equilibrium studies. *Indus. Eng. Chem. Res.*, 33: 317–320.
23. Aharoni, C. and Ungarish, M. (1977) Kinetics of activated chemisorption part 2—theoritical models. *J. Chem. Soc., Faraday Trans. I.*, 73: 456–464.