Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Removal of Lead Ions from Aqueous Solutions by Different Types of Industrial Waste Materials: Equilibrium and Kinetic Studies

Amit Bhatnagar[a]; Ajay K. Jain[a]; Ashwani K. Minocha[b]; Shailendra Singh[ac]
[a] Department of Chemistry, Indian Institute of Technology (I.I.T.) Roorkee,, Roorkee, India [b] Environmental Science & Technology Division, Central Building Research Institute (C.B.R.I.),, Roorkee, India [c] Department of Medicinal Chemistry, College of Pharmacy, University of Florida, Gainesville, Florida, USA

To cite this Article Bhatnagar, Amit , Jain, Ajay K. , Minocha, Ashwani K. and Singh, Shailendra(2006) 'Removal of Lead Ions from Aqueous Solutions by Different Types of Industrial Waste Materials: Equilibrium and Kinetic Studies', Separation Science and Technology, 41: 9, 1881 — 1892

To link to this Article: DOI: 10.1080/01496390600725828

URL: http://dx.doi.org/10.1080/01496390600725828

Separation Science and Technology, 41: 1881–1892, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600725828

Removal of Lead Ions from Aqueous Solutions by Different Types of Industrial Waste Materials: Equilibrium and Kinetic Studies

Amit Bhatnagar and Ajay K. Jain
Department of Chemistry, Indian Institute of Technology (I.I.T.) Roorkee, Roorkee, India

Ashwani K. Minocha
Environmental Science & Technology Division, Central Building Research Institute (C.B.R.I.), Roorkee, India

Shailendra Singh
Department of Chemistry, Indian Institute of Technology (I.I.T.) Roorkee, Roorkee, India and Department of Medicinal Chemistry, College of Pharmacy, University of Florida, Gainesville, Florida, USA

Abstract: A comparative study of the adsorbents prepared from several industrial wastes for the removal of Pb^{2+} has been carried out. Fertilizer industry waste viz. carbon slurry and steel plant wastes viz. blast furnace (B.F.) slag, dust, and sludge were investigated as low-cost adsorbents after proper treatment in the present study. The adsorption of Pb^{2+} on different adsorbents has been found in the order: B.F. sludge > B.F. dust > B.F. slag > carbonaceous adsorbent. The least adsorption of Pb^{2+} on carbonaceous adsorbent even having high porosity and consequently greater surface area as compared to other three adsorbents, indicates that surface area and porosity are not important factors for Pb^{2+} removal from aqueous solutions. The adsorption of Pb^{2+} has been studied as a function of contact time, concentration, and temperature. The adsorption has been found to be exothermic, and the data conform to the Langmuir equation. The kinetic results reveal that the present adsorption

Received 6 November 2005, Accepted 13 February 2006
Address correspondence to Amit Bhatnagar, (Present Address) Environmental Science & Technology Division, Central Building Research Institute (C.B.R.I.), Roorkee 247667, India. E-mail: amit_b10@yahoo.co.in

system follows Lagergren's first order rate equation. Since all three waste products from the steel industry show higher potential to remove lead from water, therefore, it is suggested that these metallurgical wastes can be fruitfully employed as low-cost adsorbents for effluent treatment containing toxic metal ions.

Keywords: Steel plant wastes, fertilizer industry waste, low-cost adsorbents, lead removal, equilibrium and kinetic studies

INTRODUCTION

The rapid pace of industrialization has led to the severe problem of water pollution. Increased awareness of toxic effects of pollutants has forced industries and municipal authorities to treat wastewater before mixing it with natural water bodies. Amongst several wastewater treatment technologies, adsorption is the most versatile process and widely used for the pollutants removal from wastewaters (1). Activated carbon has been found to be a very good adsorbent for effluent treatment and is commonly used for the removal of diverse types of pollutants. However, its widespread use in wastewater treatment is sometimes restricted due to its higher cost. As such, for quite sometime, efforts are being made to prepare cheaper adsorbents (2). However, these materials have not shown promising adsorption characteristics in comparison to activated carbon and the search is still going on.

On the other hand, solid waste materials/by-products generated from various industrial activities have become one of society's most vexing problems. In many cities of developing countries, the lack of adequate treatment of solid wastes, including industrial wastes, remains one of the major problems to be solved. One of the interesting and beneficial utilization of solid wastes (wherever possible) is to convert them into "low cost adsorbents" for the treatment of wastewater discharged from various industries. If the solid wastes could be used as low cost adsorbents, it will provide a two–fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly the low cost adsorbent if developed can reduce the pollution of wastewaters at a reasonable cost. One category of industrial wastes is "metallurgical wastes" which are available almost free of cost and cause a major disposal problem. Different metallurgical solid wastes (3–8) have been explored to serve as versatile and cost-effective adsorbents for heavy metals removal, but their efficiency in removing pollutants has been found on lower side and still the search is going on.

Among several industries, the steel industry produces a number of wastes in large quantities such as blast furnace slag, dust, and sludge. However, their utility as adsorbents for the removal of toxic metal ions has not been widely explored. Only few reports (4–8) are available dealing with the adsorption properties of these wastes. However, no report is available where efficiency of all these metallurgical wastes viz. blast furnace slag, dust, and sludge has been compared together for the removal of toxic metal ions from wastewater.

On the other hand, carbon slurry, a fertilizer industry waste, also causes serious disposal problems. It was reported in previous studies (9, 10), that carbon slurry waste after proper treatment shows higher efficiency in removing organic pollutants viz. dyes and phenols as compared to other three adsorbents (blast furnace sludge, dust and slag). But, efficacy of carbon slurry waste in removing toxic metal ions from wastewaters has not been widely explored. Further, no report is available dealing with a comparative study on the adsorption of toxic metal ions both on carbonaceous waste as well as metallurgical wastes.

Therefore, in the present communication, we have attempted to investigate the adsorption of Pb^{2+} on several metallurgical wastes viz. blast furnace sludge, dust, and slag from the steel industry and a carbon slurry waste from fertilizer plant. The results have been compared with those on standard activated charcoal in order to know the efficacy of the adsorbents developed. Lead, ubiquitous in the environment, is emitted into the environment by various activities. The toxic effects of lead are very well–documented in literature. As will be demonstrated below, metallurgical waste materials show promising results in removing Pb^{2+} from water and can be used fruitfully in treating industrial effluents containing toxic metal ions.

EXPERIMENTAL

Reagents and Materials

Lead solutions were prepared with $Pb(NO_3)_2$ and $NaNO_3$ by dissolving them into double distilled water.

Preparation of Carbonaceous Adsorbent

Carbon slurry, a waste from fertilizer plant, was used for preparing the carbonaceous adsorbent by the procedure reported previously (9–11). The dried carbon slurry in the form of cake was procured from National Fertilizer Limited (NFL), Panipat (India). Initially, it was treated with hydrogen peroxide to oxidize the adhering organic material. The further processing, which involved activation and removal of ash content by treating it with 1 M HCl and washing with distilled water, was done. The yield of the finished product was found to be ~90%. This product has been called "carbonaceous adsorbent". The adsorbent was sieved to different mesh sizes and stored in a desiccator. The optimum activation temperature, which imparts maximum adsorption property, was found to be 500°C (9).

Preparation of Blast Furnace Sludge, Dust, and Slag Adsorbents

These adsorbents were prepared from wastes obtained from Malvika Steels, Jagdishpur (India) by the method reported elsewhere (10). The products were sieved and stored in a desiccator.

Adsorption Studies

A series of batch adsorption experiments were conducted to determine adsorption of Pb^{2+} on the prepared adsorbents. For this, a fixed amount of the adsorbents (0.01 g) was added to 10 ml of lead solution of varying concentrations taken in 50 ml stoppered glass tubes, which were placed in thermostat cum shaking assembly. The solutions were stirred continuously at constant temperature to achieve equilibrium. After equilibrium, the adsorbent was allowed to settle and then filtered and this filtrate was analyzed by atomic absorption spectrophotometer to determine the equilibrium concentration of Pb^{2+}. The amount of Pb^{2+} adsorbed on the adsorbents was determined from the difference between the initial and equilibrium concentrations. The adsorption was also studied as a function of time at two concentrations in order to have kinetic information.

RESULTS AND DISCUSSION

Characterization of the Prepared Adsorbents

All the adsorbents prepared were characterized and detailed description on the characterization of prepared adsorbents can be found in previous reports (9, 10). Carbonaceous adsorbent having 89.8% carbon content was considered as "organic adsorbent" in nature. On the other hand, blast furnace (B.F.) sludge and dust having 35% and 21.7% carbon content respectively, besides other inorganic constituents were considered as "mixed type of adsorbents" in nature, where inorganic nature predominating organic in these adsorbents. Blast furnace slag was considered purely as "inorganic adsorbent" in nature as it showed high amount of inorganic constituents. These adsorbents were characterized in terms of surface area, methylene blue numbers, and iodine numbers and the results are shown in Table 1. The results reveal that carbonaceous adsorbent imparts maximum surface area (380 m^2/g), larger porosity, and higher potential to adsorb organic molecules, whereas the same characteristics were found on the lower side in other three adsorbents viz. B.F. sludge, dust, and slag.

Table 1. Characteristics of adsorbents used

	Standard activated charcoal (E. Merck)	Carbonaceous adsorbent	B.F. sludge	B.F. dust	B.F. slag
Surface area ($m^2 g^{-1}$)	710	380	28	13	4
Iodine number	635	330	24	11	3
Methylene blue number	198	90	6	3	2

The samples of carbonaceous adsorbent, slag, dust, and sludge were stirred with deionized water for 2 h and left for 24 h to see any interaction. It was seen that in case of BF slag, dust, and sludge, an enhancement of pH was observed indicating alkaline hydrolysis of inorganic constituents. In case of carbonaceous adsorbent, the pH of water was lowered, which indicates that carbonaceous adsorbent, as per Steenberg classification (12), comes under "L" type carbon. X-ray spectra of carbonaceous adsorbent does not show any peak, thereby indicating its amorphous nature. The X-ray diffraction peaks in the spectra of BF sludge and dust are due to iron oxides while in case of BF slag indicates the presence of silicates of calcium and aluminum and quartz. The IR spectra of the sample of carbonaceous adsorbent taken indicates the presence of two prominent bands lying at 1605 and 3340 cm^{-1}. The first peak may be assigned to the presence of carbonyl group and the latter one to OH group.

Effect of Contact Time and Concentration

In order to find equilibrium time for maximum adsorption and to know the kinetics of adsorption process, the adsorption of Pb^{2+} at fixed concentration on all adsorbents was studied as a function of contact time and the results are shown in Fig. 1. It is seen from this figure that rate of uptake of Pb^{2+} is rapid in the beginning and 50% adsorption is completed within 2 h. Figure 1 also indicates that the time required for equilibrium adsorption is 6 h. Thus for all equilibrium adsorption studies, the equilibration period was kept 8 h. The effect of concentration on equilibrium time was also investigated at different concentrations. It was found that the time of equilibrium as well as 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.

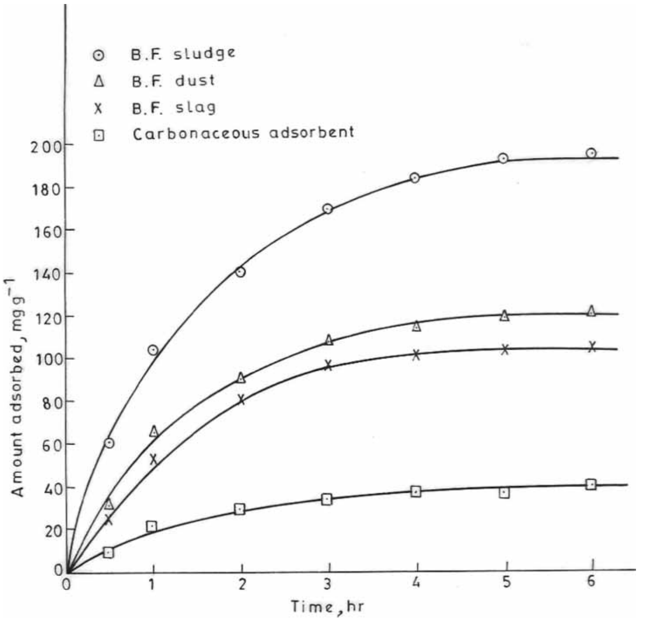

Figure 1. Effect of contact time on uptake of Pb^{2+} on different adsorbents (temperature: 25°C; particle size: 200–250 mesh).

Adsorption Isotherms

In order to determine the efficacy of the prepared adsorbents, the equilibrium adsorption studies were carried out and the adsorption isotherms are shown in Fig. 2. It is seen from Fig. 2 that Pb^{2+} adsorption is greater on BF sludge, dust, and slag which have lower porosity and consequently lower surface area as compared to carbonaceous adsorbent. The results clearly indicate that for the adsorption of Pb^{2+} on blast furnace sludge, dust, and slag, the surface area and porosity are not important factors. The mechanism of Pb^{2+} adsorption onto the surface of blast furnace wastes is a complex process which may involve different processes such as ion exchange, surface precipitation and/or surface complex formation. López and coworkers (13) while studying the adsorption of Pb^{2+} on blast furnace sludge, suggested that Pb^{2+} fixation on the sludge surface occurs, at least partially, by replacement of other cations such as Ca^{2+}. Dimitrova (14) studied the use of granulated blast furnace slag (GBFS) for lead removal and stated that the apparent mechanisms of lead removal in GBFS column are sorption (ion exchange and adsorption) and precipitation. However, besides the above mechanisms, it is also possible that other mechanisms such as surface complex formation (15) etc. may take place simultaneously depending upon the nature of adsorbent and experimental conditions.

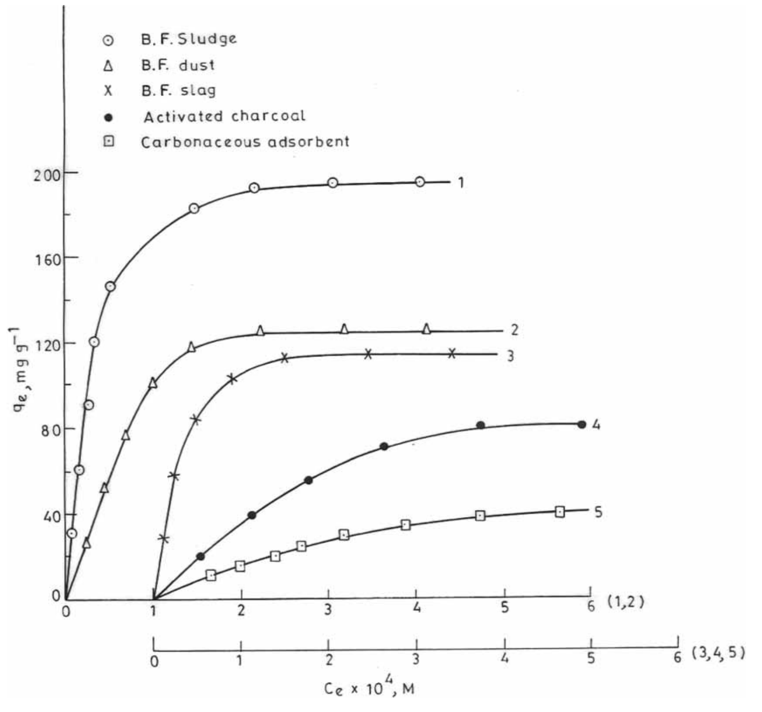

Figure 2. Adsorption isotherm of Pb^{2+} on different adsorbents at 25°C (particle size: 200–250 mesh).

On the other hand, the adsorption of Pb^{2+} on carbonaceous adsorbent appears due to physical effects as a result of large surface area and porosity of this adsorbent. However, compared to other three adsorbents, carbonaceous adsorbent exhibits least adsorption of Pb^{2+}.

Further, adsorption of Pb^{2+} on these adsorbents was compared with standard activated charcoal and the results are shown in Fig. 2. It is clear from the figure that even as compared to activated charcoal, the blast furnace sludge, dust, and slag show more adsorption of Pb^{2+}, again indicating that surface area role is not predominant. However, compared to carbonaceous adsorbent ($q_m = 40\,\text{mg/g}$), activated charcoal ($q_m = 80\,\text{mg/g}$) adsorbs almost twice.

Effect of Temperature

To determine the effect of temperature on the adsorption of Pb^{2+}, experiments were also conducted at 45°C and results are shown in Fig. 3. A comparison of adsorption isotherms at 25° and 45°C shows that adsorption decreases with

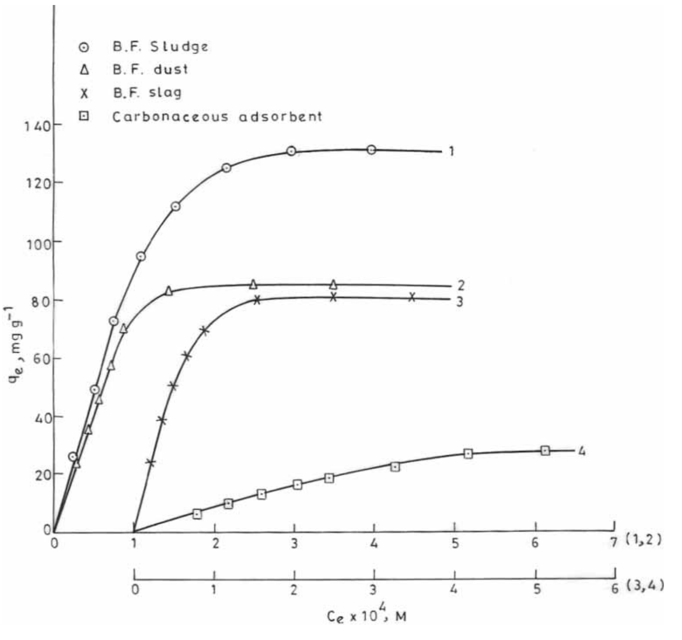

Figure 3. Adsorption isotherm of Pb^{2+} on different adsorbents at 45°C (particle size: 200–250 mesh).

increase in temperature indicating that the adsorption of Pb^{2+} is exothermic. The adsorption data was further analyzed and found to conform best to following Langmuir equation

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

where 'q_e' is the amount adsorbed at equilibrium concentration 'C_e', 'q_m' the Langmuir constant representing maximum monolayer capacity and 'b' the Langmuir constant related to energy of adsorption. The plots between $1/q_e$ and $1/C_e$ for the adsorption of Pb^{2+} on carbonaceous adsorbent are drawn in Fig. 4. Similar plots were also obtained for other adsorbents. The values of monolayer capacity (q_m) and Langmuir constant (b) have been evaluated from the intercept and slope of these plots and given in Table 2. A perusal of Table 2 shows that monolayer capacity (q_m) of the adsorbent for Pb^{2+} is comparable to the maximum adsorption obtained from adsorption isotherms (Figs. 2 and 3). As 'b' values reflect equilibrium constant for the adsorption process, it shows the affinity of the adsorbent for Pb^{2+}. Thus, 'b' values indicate that B.F. sludge has maximum affinity for Pb^{2+} and carbonaceous adsorbent has minimum affinity for Pb^{2+}. This is consistent with our experimental results obtained that amount adsorbed of Pb^{2+} on different adsorbents is in the order: B.F. sludge > B.F. dust > B.F. slag > carbonaceous adsorbent.

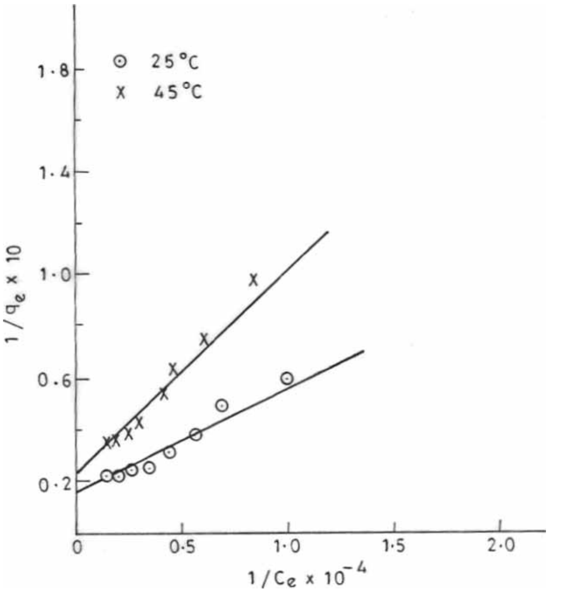

Figure 4. Langmuir adsorption isotherms of Pb^{2+} on carbonaceous adsorbent at different temperatures.

Dynamic Modelling

Kinetics of sorption is one of the important characteristics in defining the efficiency of sorption. Various kinetic models have been proposed by various workers where the adsorption has been treated as first order (16, 17), pseudo first order (18, 19), and pseudo second order process (20). Different

Table 2. Langmuir adsorption parameters of Pb^{2+} adsorption on different adsorbents

Adsorbent	Temp. (°C)	q_m (mg g^{-1})	b (L mol^{-1})
B.F. sludge	25	227	2.47×10^4
	45	161	1.03×10^4
B.F. dust	25	142	1.75×10^4
	45	111	0.64×10^4
B.F. slag	25	125	1.56×10^4
	45	91	0.57×10^4
Carbonaceous adsorbent	25	55	0.33×10^4
	45	45	0.28×10^4

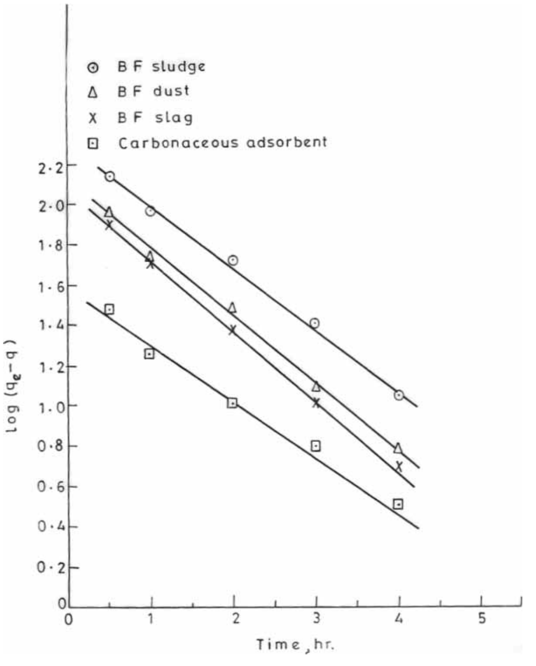

Figure 5. Lagergren's plots for Pb^{2+} on different adsorbents.

systems conform to different models. The Lagergren's rate equation (21) is the one most widely used (16, 17, 22) for the sorption of a solute from a liquid solution. Thus this first order equation:

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

where 'q_e' and 'q' are amount of Pb^{2+} 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 Pb^{2+} 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. 5. The plots were found to be linear indicating that Lagergren's equation is applicable to the present Pb^{2+} adsorption studies on prepared adsorbents and the adsorption is a first order process.

Environmentally-safe Disposal of Metal-laden Adsorbents

The experiments for the ultimate disposal of Pb^{2+}-laden adsorbents by cement-fixation were performed. The preliminary results indicate that the solidified cement blocks did not show any significant leaching of fixed metal ion (Pb^{2+}) over extended period of time under different environmental conditions.

CONCLUSION

In this work, we have tackled the problem of pollution with two-fold objectives:

1. First, utilized various industrial wastes of fertilizer industry and steel industry by converting them into low-cost adsorbents after proper treatment; and
2. Secondly, used these low-cost adsorbents for the removal of toxic metal ions (Pb^{2+} in this study) from wastewater through adsorption process.

A comparative study between wastes of fertilizer plant and steel industry clearly shows that metallurgical waste products from steel plant can be fruitfully employed for the removal of divalent metal ions from wastewater at a reasonable cost. Thus, the proposed technology offers a two-fold objective of solid waste management and wastewater treatment.

ACKNOWLEDGEMENT

The authors are thankful to Ministry of Environment and Forests, Government of India for financial support.

REFERENCES

1. Faust, S.D. and Aly, O.M. (1987) *Adsorption Process for Water Treatment*; Butterworths Publishers: Stoneham.
2. Bailey, S.E., Olin, T.J., Bricka, R.M., and Adrian, D.D. (1999) A review of potentially low-cost sorbents for heavy metals. *Water Res.*, 33 (11): 2469–2479.
3. Lopez, E., Soto, B., Arias, M., Nunez, A., Rubinos, D., and Barral, M.T. (1998) Adsorbent properties of red mud and its use for wastewater treatment. *Water Res.*, 32 (4): 1314–1322.
4. Yamada, H., Kayama, M., Saito, K., and Hara, M. (1986) A fundamental research on phosphate removal using slag. *Water Res.*, 20 (5): 547–557.
5. Dimitrova, S.V. (1996) Metal sorption on blast-furnace slag. *Water Res.*, 30 (1): 228–232.
6. López-Delgado, A., Pérez, C., and López, F.A. (1998) Sorption of heavy metals on blast furnace sludge. *Water Res.*, 32 (4): 989–996.
7. Jallan, G. and Pandey, G.S. (1992) Blast furnace gas cleaning sludge as adsorbent of some toxic ions. *Res. Ind.*, 37: 143–145.
8. Patnaik, L.N. and Das, C.P. (1995) Removal of hexavalent chromium by blast furnace flue dust. *Ind. J. Environ. Health.*, 37 (1): 19–25.

9. Jain, A.K., Suhas, Jain, S., and Bhatnagar, A. (2001) Utilization of industrial wastes for the removal of anionic dyes. *Toxicol. Environ. Chem.*, 84 (1–4): 41–52.
10. Jain, A.K., Suhas, and Bhatnagar, A. (2002) Methylphenols removal from water by low-cost adsorbents. *J. Colloid Interface Sci.*, 251: 39–45.
11. Srivastava, S.K., Pant, N., and Pal, N. (1987) Studies on the efficiency of a local fertilizer waste as low cost adsorbent. *Water Res.*, 21 (11): 1389–1394.
12. Mattson, J.S. and Mark, H.B., Jr. (1972) *Activated Carbon Surface Chemistry and Adsorption from Solutions*; Marcel Dekker, Inc.: New York.
13. López, F.A., Perez, C., Sainz, E., and Alonso, M. (1995) Adsorption of Pb^{2+} on blast furnace sludge. *J. Chemical Technol. Biotechnol.*, 62: 200–206.
14. Dimitrova, S.V. (2002) Use of granular slag columns for lead removal. *Water Res.*, 36: 4001–4008.
15. Farley, K.J., Dzombak, D.A., and Morel, M.M. (1985) A surface precipitation model for the sorption of cations on metal oxides. *J. Colloid Interface Sci.*, 106: 226–242.
16. Panday, K.K., Prasad, G., and Singh, V.N. (1985) Copper(II) removal from aqueous solutions by fly ash. *Water Res.*, 19: 869–873.
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: 2315–2324.
19. Ho, Y.S. and McKay, G. (1999) The sorption of lead(II) ions on peat. *Water Res.*, 33: 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: 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. (1994) Process development for removal and recovery of cadmium from wastewater by a low-cost adsorbent: Adsorption rates and equilibrium studies. *Ind. Eng. Chem. Res.*, 33: 317–320.