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

Removal of Nickel(II) and Zinc(II) from Wastewater Using Fly Ash and Impregnated Fly Ash

S. S. Banerjee[a]; R. V. Jayaram[a]; M. V. Joshi[b]
[a] Applied Chemistry Division, Department of Chemical Technology, University of Mumbai, Matunga, Mumbai, India [b] ICI India Research & Technology Center, Thane, India

To cite this Article Banerjee, S. S. , Jayaram, R. V. and Joshi, M. V.(2003) 'Removal of Nickel(II) and Zinc(II) from Wastewater Using Fly Ash and Impregnated Fly Ash', Separation Science and Technology, 38: 5, 1015 — 1032
To link to this Article: DOI: 10.1081/SS-120018121
URL: http://dx.doi.org/10.1081/SS-120018121

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 5, pp. 1015–1032, 2003

Removal of Nickel(II) and Zinc(II) from Wastewater Using Fly Ash and Impregnated Fly Ash

S. S. Banerjee,[1] R. V. Jayaram,[1,*] and M. V. Joshi[2]

[1]Applied Chemistry Division, Department of Chemical Technology,
University of Mumbai, Matunga, Mumbai, India
[2]ICI India Research & Technology Center, Thane, India

ABSTRACT

Adsorption of toxic metal ions like Ni(II) and Zn(II) on fly ash and impregnated fly ash was studied in terms of different parameters like initial metal ion concentrations, pH, and temperature. Impregnated fly ash showed much higher levels of adsorption capacity for Ni(II) and Zn(II) as compared to untreated fly ash. The various rate parameters governing the adsorption process have been determined at different temperatures. Equilibrium modeling has been carried out using Langmuir isotherm equations, and the corresponding constants have been evaluated. Thermodynamic studies have also been carried out and values of standard free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) calculated. The adsorption was found to be exothermic for Ni(II) and endothermic in case of Zn(II) as determined by the values of enthalpy change.

---

*Correspondence: R. V. Jayaram, Applied Chemistry Division, Department of Chemical Technology, University of Mumbai, Matunga, Mumbai-400 019, India; Fax: +91-22-414 56 14; E-mail: ssb_rvj@aplchem.udct.ernet.in.

DOI: 10.1081/SS-120018121 0149-6395 (Print); 1520-5754 (Online)

www.dekker.com

Key Words: Ni(II); Zn(II); Fly ash; Impregnated fly ash; Adsorption isotherm.

INTRODUCTION

Rapid industrialization and the increase in the world population have contributed to heavy metal pollution in the ecosystem. Ni(II) and Zn(II) are highly toxic as they are carcinogens and mutagens in nature.[1] Ni(II) ions are released in wastewaters from metal-plating operations, silver refining, acid mine drainage, steel and printing works, and motor vehicle and aircraft industries. Zn(II) gains access to the aquatic environment from mining operations, wastewaters of electroplating, corrosion of galvanized piping, and dezincification of brass, besides other industrial waste. To curtail heavy metal pollution problems, many processes have been developed that include chemical precipitation, electrode deposition, solvent extraction, ion exchange, activated carbon adsorption,[2,3] and biological methods.[4] The main limitations of these techniques are their low efficiency in metal ion removal at trace levels or the high cost. Hence adsorption is reported to be the most effective method for this purpose, which works at low concentration.[5]

In recent years, research interest has increased in terms of production of low-cost alternatives to activated carbon, which remains an expensive material in spite of its prolific use. Fly ash is a solid waste produced in large quantities during the burning of municipal waste, fossil fuel, and coal in thermal power plants which discharge several million tons of fly ash per year. The huge deposits of fly ash around thermal power plants pose problems in disposal. Besides its utilization in preparing bricks, portland cement, etc., fly ash has also been used in wastewater treatment.[6]

The aim of the present investigation is to compare sorption of Ni(II) and Zn(II) on fly ash (FA) and impregnated fly ash (IFA) in aqueous medium.

EXPERIMENTAL

All chemicals used were of analytical grade (E. Merck, India). Stock solutions of $NiCl_2$ and $ZnSO_4$ were prepared in double-distilled water. pH measurements were carried out with an Elico digital pH meter (model No LI-120). The concentrations of Ni(II) and Zn(II) were determined on a GBC-911A (Australia) UV–visible spectrometer. The average particle size was measured with the Coulter LS 230 particle size analyzer.

Material Development

Fly ash was obtained from the Thermal Power Plant of Century Rayon, Shahad (Maharashtra). This was passed through standard test sieve No. 150, which has an average particle diameter of 100 μm. The uniform sample of fly ash thus obtained was impregnated with 0.1 M $Al(NO_3)_3$ or 0.1 M $Fe(Cl)_3$.[7] These are denoted as IFAAl and IFAFe, respectively.

Adsorption Studies

Adsorption studies were carried out using a series of Erlenmeyer flasks (250-ml capacity). The effect of pH was studied by adjusting the same with 0.1 M HCl and 0.1 M NaOH and exposing the solution to the adsorbents (FA, IFAAl, and IFAFe). After 1 hour of shaking on an orbital shaker (100 rpm), the solutions were centrifuged, and the concentrations of Ni(II) and Zn(II) were determined in the supernatant using DMG method set at a wavelength of 445 nm and mureoxide method set at wavelength of 460 nm, respectively.[8,9]

Kinetic Studies

For kinetic measurements, experiments were carried out by shaking 1 g of the adsorbent (FA, IFAAl, IFAFe) with 800 ml of Ni(II) solution or 700 ml of Zn(II) solution containing known concentration of the metal ions, in a fully baffled reactor fitted with an overhead stirrer (100 rpm) and a temperature controller (± 2°C). The pH of the solution was adjusted and maintained throughout. After definite intervals of time the adsorbent was separated from the solution by centrifuging at 8000 rpm for 10 min, and the supernant liquid was analyzed for Ni(II) and Zn(II) spectrophotometrically.

RESULTS AND DISCUSSION

Characterization of the Adsorbents

FA was found to be stable in water, dilute acids, and bases. Neither of the metal ions (Al^{3-}, Fe^{3+}) was eluted from IFA with cold or hot water or cold dil HCl but was eluted with hot dil HCl. The constituent of FA analyzed by standard method was found to contain mainly SiO_2 (52%), Al_2O_3 (27%), Fe_2O_3 (6%), CaO (0.11%), MgO (0.70%), and TiO_2 (1.01%).[10] The d-spacing values (X-ray diffraction) reveal the presence of hematite, mullite, α-quartz, γ-alumina, magnetite, and geothite. The loss in weight on ignition was found to be 13%. The loss of moisture evaluated at 110°C for 4 hours was found to be 0.9%. The average particle size was 47.9 μm for FA, 55.87 μm for IFAAl, and 50.11 μm for IFAFe.

Effect of Initial Concentration of Metal Ion

The adsorption experiments were carried out in the concentration range of 12–30 ppm for Ni(II) at pH 6.0 and 10–30 ppm for Zn(II) at pH 6.5 at 30°C. The equilibrium was established in 20 min for Ni(II) and 45 min for Zn(II), and the equilibration period was found to be independent of initial metal ion concentration. As the initial concentration of Ni(II) increased, the amount adsorbed on FA, IFAAl, and IFAFe decreased from 66.67% to 45.42%, 70.83% to 59.58%, and 69.79% to 50.0%, respectively. Similarly, the amount of Zn(II) adsorbed on FA, IFAAl, and IFAFe decreased from 50.0% to 40.48%, 65.71% to 45.24%, and 72.86% to 48.10%, respectively, as the concentration of the solution was increased.

Effect of Contact Time and Temperature

The adsorption studies were carried out at three different temperatures: 30, 45, and 60°C. With increase in temperature from 30–60°C, adsorption of Ni(II) by FA and IFAFe decreased, while for Zn(II) it increased with an increase in solution temperature and at a adsorbate concentration of 20 ppm and a pH of 6.0 for Ni(II) and 6.5 for Zn(II) (Figs. 1–4). The equilibrium time is independent of solution temperature. The same trend was observed for IFAAl as well. In this case the removal of Ni(II) decreased from 10.3 mg/g to 7.3 mg/g, and the removal of Zn(II) increased from 6.5 mg/g to 12.7 mg/g. The observations indicate the adsorption to be exothermic for Ni(II) and endothermic on Zn(II) on all three adsorbents.

ADSORPTION KINETICS

The adsorption of Ni(II) and Zn(II) can be considered as a reversible reaction. With the reaction in both directions being first order, the rate equation may be expressed as[11]:

$$\log(q_e - q) = \log q_e - K^1/2.303 \times t$$

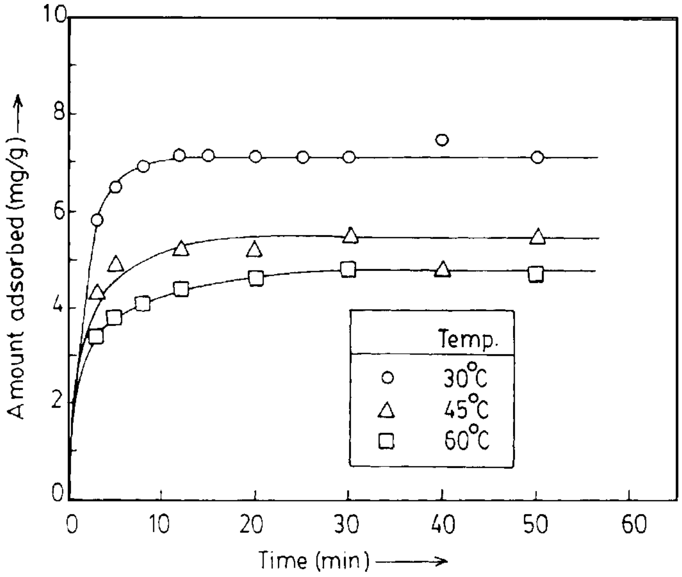

Figure 1. Effect of contact time and temperature on the Ni(II) uptake by FA.

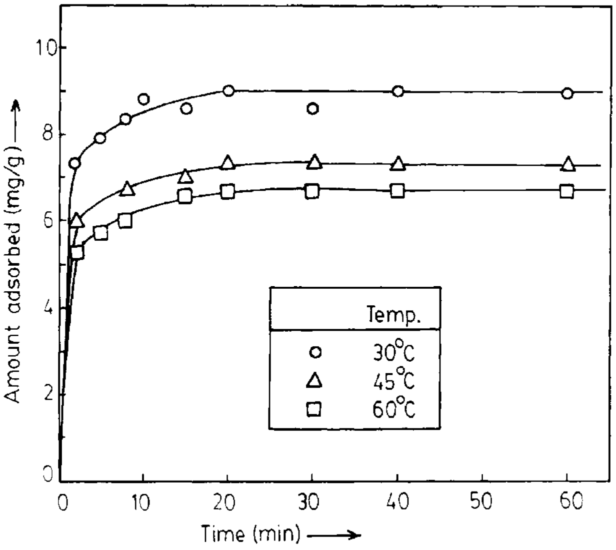

Figure 2. Effect of contact time and temperature on the Ni(II) uptake by IFAFe.

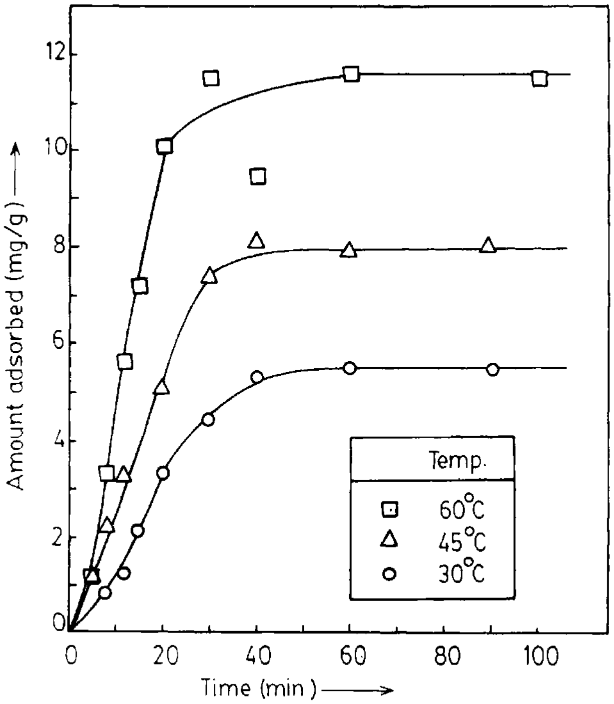

Figure 3. Effect of contact time and temperature on the Zn(II) uptake by FA.

where

q = Amount (mg/g) adsorbed at time t.

q_e = Amount (mg/g) adsorbed at equilibrium.

and

$$k^1 = k_1(1 + 1/Kc) = k_1 + k_2$$

and

$$K_c = C_{ae}/C_{se} = k_1/k_2$$

k^1 = Overall rate constant.

k_1, k_2 = Rate constants of forward and reverse reactions.

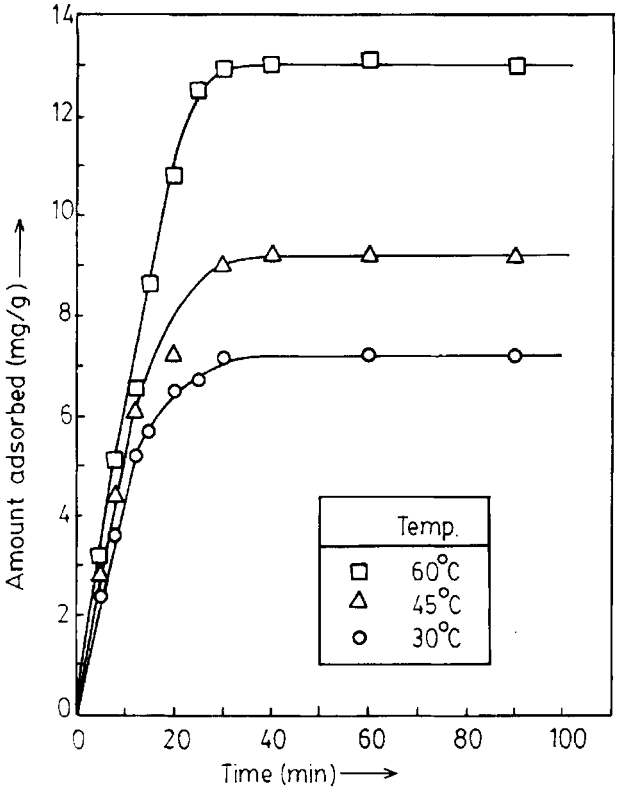

Figure 4. Effect of contact time and temperature on the Zn(II) uptake by IFAFe.

C_{ae} = equilibrium concentration (mg/dm^3) of Ni(II) or Zn(II) on the adsorbent.
C_{se} = equilibrium concentration (mg/dm^3) of Ni(II) or Zn(II) in the solution.

The overall rate constant of adsorption at different temperatures was determined from the slopes of the straight line plots of $\log(q_e - q)$ versus t (Table 1). The observation indicates that removal of Ni(II) is favored at low temperature, while that of Zn(II) is favored at high temperature.

On porous adsorbents (FA, IFAAl, and IFAFe), pore diffusion is expected in addition to surface adsorption. Hence rate constants of intraparticle transport (K_{id}) were calculated from the slopes of the linear portion of the plots of amount adsorbed versus square root of time at different temperatures[12]

Table 1. Values of rate constants at different temperatures.

	k^1 (min^{-1})					
	Ni(II)			Zn(II)		
Temp (°C)	FA	IFAAl	IFAFe	FA	IFAAl	IFAFe
30	0.299	0.391	0.332	0.104	0.108	0.120
45	0.138	0.207	0.159	0.161	0.173	0.184
60	0.097	0.111	0.101	0.184	0.196	0.214

(Table 2), from the following relationship:

$$q = K_{id} t^{0.5}$$

The initial curved portion and the linear portion of these plots are known to represent boundary layer adsorption and pore diffusion, respectively.[12] It is clear from Table 2 that the rate constant for pore diffusion (K_{id}) decreases for Ni(II) and increases for Zn(II) with rise in solution temperature. The boundary layer thickness decreases with temperature due to the increased relative escaping tendency of Ni(II) from the solid phase to bulk phase,[13] and thus, as a result of an increase in the kinetic energy of the adsorbate species, a decrease in adsorption is observed. The increase in the uptake of zinc with temperature may be due to increase in active surface centers available for adsorption, desolvation of the adsorbing species, or enhanced rate of intraparticle diffusion.[14]

The pore diffusion coefficients (Table 3) of Ni(II) and Zn(II) within the pores of adsorbents were determined assuming spherical geometry of the adsorbent using the following equation[11]:

$$D = 0.03 r_o^2 / t_{1/2}$$

Table 2. Values of pore diffusion rate constant at different temperatures.

	K_{id} ($mg\,g^{-1}\,min^{-0.5}$) $\times 10^{-2}$					
	Ni(II)			Zn(II)		
Temp (°C)	FA	IFAAl	IFAFe	FA	IFAAl	IFAFe
30	30.0	72.73	57.14	15.0	25.0	33.3
45	22.20	60.0	33.30	21.70	30.76	35.0
60	18.18	41.67	40.0	40.0	55.56	75.0

Table 3. Values of activation energy and diffusion coefficients of Ni(II) and Zn(II).

	Ea (kJ mol^{-1})			Diffusion coefficient D (m^2 s^{-1}) × 10^{-12}		
	FA	IFAAl	IFAFe	FA	IFAAl	IFAFe
Ni(II)	9.94	4.98	7.47	6.88	9.36	7.53
Zn(II)	24.90	19.95	11.60	3.06	4.16	3.35

where r_o is the radius of the adsorbent, D is the pore diffusion coefficient (m^2 s^{-1}), and $t_{1/2}$ is the time for half adsorption. The determined values of the pore diffusion coefficients are on the order of 10^{-12}, and these low values suggest that the pore diffusion is the rate-limiting step.[15]

The energy of activation was determined from the slope of the Arrhenius plots (Table 3).

Effect of Impregnation by Al^{3+} and Fe^{3+} Ions

In comparison with FA the extent of adsorption of Ni(II) and Zn(II) is higher for IFA (Figs. 5 and 6). This is probably caused by the newly developed active sites (Al-OH or Fe-OH layers) formed due to the electrostatic interaction between $Al(OH)_3$, $Fe(OH)_3$, and SiO_2 on IFA.[16] Adsorbents with a surface layer of Al-OH can specifically adsorb metal cations. The pH-dependent charge is suggested to be located at the edge sites, where the surface hydroxyl groups can be protonated or deprotonated depending on the pH.[17,18] Small heavy metal cations can be bound specifically by the edge hydroxyl groups of the Al or Fe in the hydroxide surface layer on the planar surfaces of the modified fly ash. The low-affinity sites on the permanently charged surface are widely replaced by high-affinity Al(OH) functional groups with variable charge.[19] This is supported also by the fact, that, as compared to pure FA, the dissolved concentrations of Ni(II) and Zn(II) are increased at low pH values when FA is treated with Al or Fe (Figs. 7 and 8).

Langmuir Adsorption Isotherm

The values obtained from the adsorption studies of Ni(II) and Zn(II) on FA, IFAAl, and IFAFe were well fitted in the rearranged Langmuir equation:

$$C_e/q_e = 1/Q_o b + C_e/Q_o$$

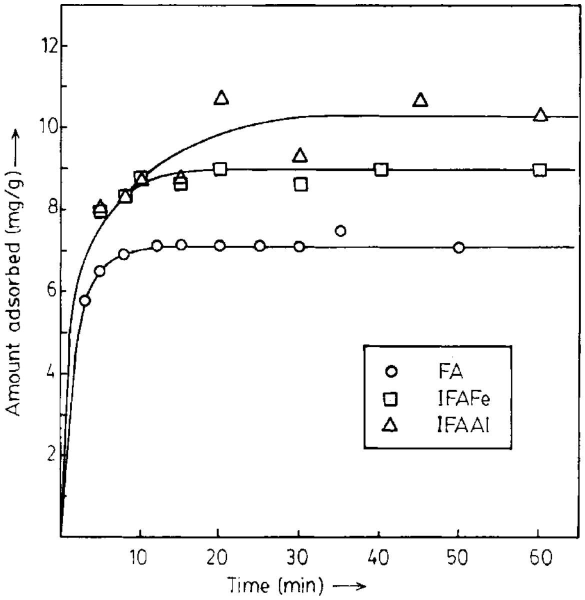

Figure 5. Adsorption kinetic of Ni(II) on untreated and treated fly ash.

where

C_e = Equilibrium concentration (mg dm^{-3})
Q_0, b = Langmuir constants

The values of Q_o and b (Table 4) were determined at various temperatures.

Thermodynamic Parameters

The various thermodynamic parameters were calculated with the help of standard equations.[20]

$$\Delta G^0 = -RT\ln Kc$$

$$\Delta H^0 = R(T_2T_1)/(T_2 - T_1)\ln(Kc_2/Kc_1)$$

$$\Delta S^0 = (\Delta H^0 - \Delta G^0)/T$$

Kc_1, Kc_2 = Equilibrium constants at T_1 and T_2

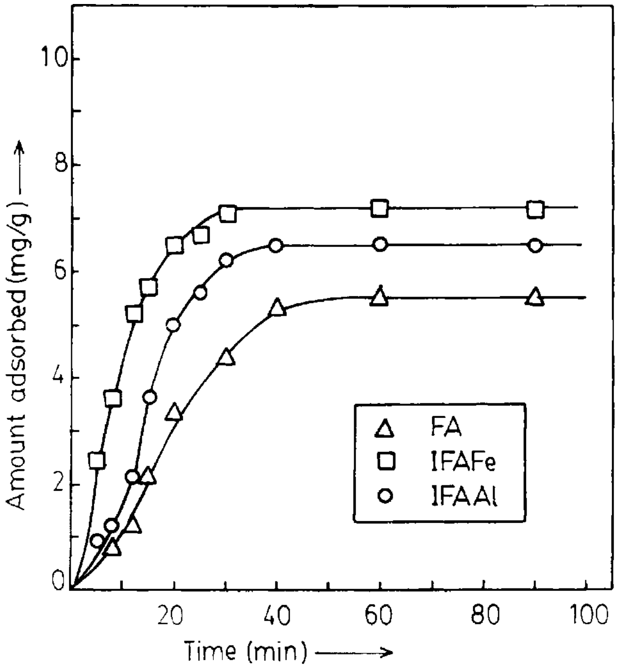

Figure 6. Adsorption kinetic of Zn(II) on untreated and treated fly ash.

The free energy increases with increase in temperature for Ni(II), which indicates an increase in adsorption at lower temperatures, but in case of Zn(II), it shows a reverse trend, indicating an increase in adsorption at higher temperature. The negative value of ΔG^0 in case of Ni(II) and Zn(II) adsorption on IFAAl and IFAFe at lower temperatures suggest the process to be spontaneous in contrast to FA (Tables 5 and 6). The negative value of ΔH^0 for Ni(II) suggests the exothermic nature of the adsorption process, and the positive ΔH^0 for Zn(II) suggests an endothermic adsorption (Tables 4 and 5).

Effect of pH

The removal of pollutants from wastewaters by adsorption is highly dependent on pH, which affects the surface charge of the adsorbent, and the degree of ionization and specification of the adsorbate.[21] The plots of amount adsorbed at equilibrium at various pH values are as shown in Figs. 7 and 8.

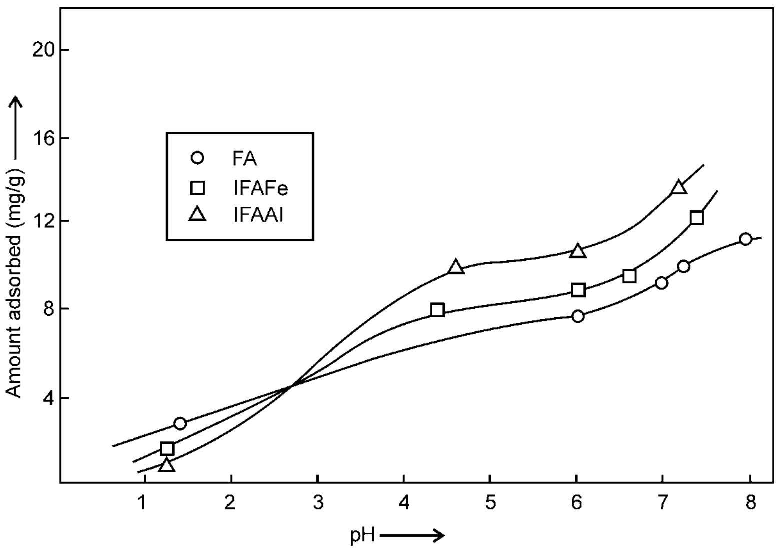

Figure 7. Effect of pH on the amount of Ni(II) uptake of FA, IFAAl, and IFAFe.

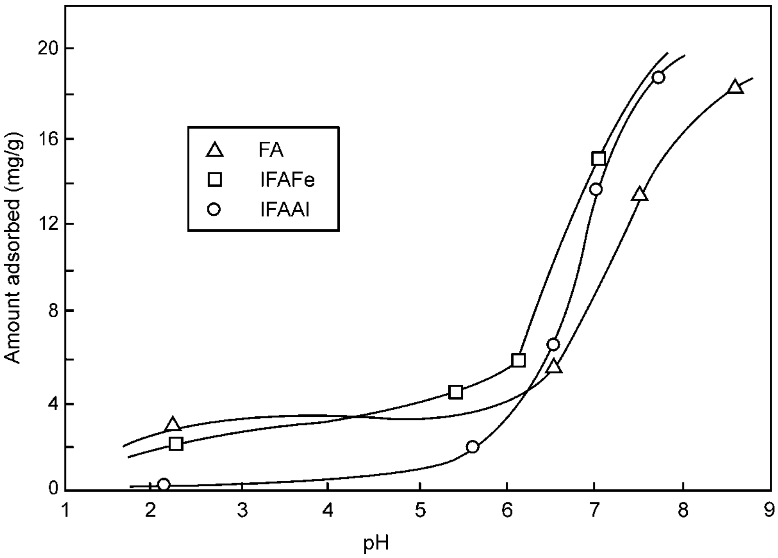

Figure 8. Effect of pH on the amount of Zn(II) uptake of FA, IFAAl, and IFAFe.

Table 4. Values of Langmuir constants.

	$\mathbf{Q_o}$ (mg g^{-1})						$\mathbf{b}$ (dm^3 mg^{-1}) × 10^{-2}					
	Ni(II)			Zn(II)			Ni(II)			Zn(II)		
Temp (°C)	FA	IFAAl	IFAFe	FA	IFAAl	IFAFe	FA	IFAAl	IFAFe	FA	IFAAl	IFAFe
30	14.0	15.75	14.93	6.49	7.0	7.50	8.0	13.0	9.0	15.4	20.0	27.0
45	9.0	13.70	12.01	10.0	10.64	11.50	7.40	12.10	8.30	17.0	21.0	29.0
60	7.19	10.0	9.80	13.33	15.39	15.50	7.0	11.30	7.9	18.8	22.0	32.0

Table 5. Thermodynamic parameters at different temperatures for Ni(II).

Temp (°C)	ΔG^0 (kJ mol^{-1})			ΔH^0 (kJ mol^{-1})			ΔS^0 (kJ mol^{-1} K^{-1})		
	FA	IFAAl	IFAFe	FA	IFAAl	IFAFE	FA	IFAAl	IFAFe
30	0.444	− 1.492	− 0.444	− 22.48	− 24.92	− 22.79	− 0.076	− 0.077	− 0.077
45	1.851	− 0.331	0.465	− 6.759	− 17.65	− 8.96	− 0.027	− 0.054	− 0.030
60	2.430	0.486	0.908	—	—	—	—	—	—

Table 6. Thermodynamic parameters at different temperatures for Zn(II).

	ΔG^0 (kJ mol^{-1})			ΔH^0 (kJ mol^{-1})			ΔS^0 (kJ mol^{-1} K^{-1})		
Temp (°C)	FA	IFAAl	IFAFe	FA	IFAAl	IFAFe	FA	IFAAl	IFAFe
30	1.097	0.360	−0.144	38.63	32.51	31.71	0.124	0.106	0.105
45	−0.761	−0.294	−1.716	37.81	27.33	8.66	0.121	0.086	0.033
60	−4.365	−6.305	−7.105	—	—	—	—	—	—

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

At low pH values, hydrogen ions compete with Ni(II) and Zn(II), and the percentage removal of metal ion is low.[22] With increasing pH the adsorbent surface contains more of AlO^- and SiO^- species, which bind electrostatically with Ni(II) and Zn(II) ions, thereby resulting in an enhancement in adsorption.

Application of the Developed Adsorption System

The developed IFA are very effective, economical, and rapid for the removal of Ni(II) and Zn(II). This system has successfully been tested to remove Ni(II) and Zn(II) from wastewater obtained from an electroplating plant, MIDC, Badlapur (Maharashtra). It was observed that the system is capable of removing these two metal ions up to 90–95%. Hence the system can be developed and extended for further practical applications of wastewater treatment.

Desorption studies of Ni(II) and Zn(II) adsorbed on IFAAl and IFAFe from wastewater were also performed. Approximately 12.0% and 11.67% of Ni(II) or 13.2% and 12.42% of Zn(II) were eluted from IFAAl and IFAFe when adsorbents loaded with Ni(II) or Zn(II) were placed in a highly acidic medium of pH 2.11 under agitation (100 rpm) for 1 hour at 30°C.

Since the metal ions would not leach out once retained, the metal loaded adsorbents can ultimately be disposed of by solidification and stabilization procedures, without fear of leaching and environmental hazard. In fact it had been observed, when metal-loaded solid FA was added up to 20% by mass to Portland cement-based formulations, the fixed metals did not leach out from the solidified concrete blocks over extended periods.[23]

The IFAAl and IFAFe loaded with Ni(II) and Zn(II) can be used for soil amendment to raise food crops, without any risk of trace element pollution, as has been successfully achieved with FA.[24]

CONCLUSIONS

On the basis of the presented results, the following inferences can be drawn:

1) The sorption capacity of IFA is higher than that of FA.
2) The rise in the solution temperature does not favor Ni(II) removal but favors that of Zn(II).

3) The negative value of ΔG^0 in case of Ni(II) and Zn(II) adsorption on IFAAl and IFAFe at lower temperature suggests the process to be more spontaneous as compared to FA.
4) FA and IFA show enhanced adsorption at higher pH values.

REFERENCES

1. Moore, J.W.; Ramamoorthy, S. *Heavy Metals in Natural Waters: Applied Monitoring and Impact Assessment*; Springer: New York, 1984; 69.
2. Dean, J.G.; Bosqui, F.L. Removing heavy metals from wastewater. Environ. Sci. Technol. **1972**, *6*, 518.
3. Argman, Y.; Weddle, C.L. Fate of heavy metals from in physical–chemical treatment processes. Am. Inst. Chem. Eng. Symp. Ser. Wat. **1973**, *70* (136), 400.
4. Neufeld, R.D.; Hermann, E.R. Heavy metal removal by activated sludge. J. Water Pollut. Control Fed. **1975**, *47*, 310.
5. Weltrowski, M.; Martel, B.; Morcellet, M. Chitosan N-benzyl sulfonate derivatives as sorbents for the removal of metal ions in an acidic medium. J. Appl. Polym. Sci. **1996**, *59*, 647.
6. Jain, K.K.; Singh, V.N.; Prasad, G. Applications of fly ash instead of activated carbon for oxalic acid removal. J. Chem. Technol. Biotechnol. **1979**, *29*, 36.
7. Rathore, H.S.; Sharma, S.K.; Agarwal, M. Adsorption of some organic acids on fly ash impregnated with hydroxides of Al, Cd, Cu, Fe and Ni. Environ. Pollut. (Ser. B) **1985**, *10*, 249.
8. Sandell, E.B. *Colorimetric Determination of Traces of Metals*; Interscience Pub.: New York, 1944.
9. Tare, M.; Zaki, M.; Raagheb, A.-G.; Mohamed, A.S. Determination of zinc in aluminum metal and alloys using a sensitized murexide reaction. J. Chem. Technol. Biotechnol. **1990**, *48*, 127.
10. Vogel, A.I. *Text Book of Qualitative Chemical Analysis*, 5th Ed.; ELBS Publication: London, 1989.
11. Bhattacharya, A.K.; Venkobachar, C. Removal of cadmium(II) by low cost adsorbents. J. Environ. Eng. **1984**, *110* (1), 110.
12. Weber, W.J.; Morris, J.C. Kinetic of adsorption on carbon on solution. J. Sanit. Eng. Div. ASCE **1963**, *89* (SA2), 31.
13. Yadava, K.P.; Tyagi, B.S.; Singh, V.N. Fly ash for the treatment of water enriched in lead (II). J. Environ. Sci. Health **1989**, *A24* (7), 783.

14. Knocke, W.R.; Hemphill, L.H. Mercury sorption by waste rubber. Water Res. **1981**, *15*, 275.
15. Michelson, L.D.; Gideon, P.G.; Pace, E.G.; Kutal, L.H. *Removal of Soluble Mercury from Waste Water by Complexing Technique*; Bull. No. 74; US Dept. Industry, Office of Water Research and Technology, 1975.
16. Meng, X.; Letterman, R. Modeling ion adsorption on aluminium hydroxide modified silica. Environ. Sci. Technol. **1993**, *27*, 1924.
17. Harsh, J.B.; Doner, H.E. Specific adsorption of copper on an hydroxy aluminum–montmorillonite complex. Soil. Sci. Soc. Am. J. **1984**, *48*, 1034.
18. Keisar, P.; Bruggenwert, M.G.M. In *Interactions at the Soil Colloid–Soil Solution Interface*; Bolt, G.H., De boodt, M.F., Hayes, M.H.B., McBride, M.B., Eds.; Kluwer Academic Publisher: Dordrecht, 1991; 177.
19. Lothenbach, B.; Furrer, G.; Schulin, R. Immobilization of heavy metal by polynuclear aluminium and montmorillonite compounds. Environ. Sci. Technol. **1997**, *31*, 1452.
20. Yadava, K.P.; Tyagi, B.S.; Singh, V.N. Effect of temperature on the removal of lead(II) by adsorption on china clay and wollastonite. J. Chem. Technol. Biotechnol. **1991**, *51*, 47.
21. Elloit, H.A.; Huang, C.P. Adsorption characteristic of some Cu(II) complexes on alumino silicates. Water Res. **1981**, *15*, 849.
22. Gupta, G.S.; Singh, A.K.; Tyagi, B.S.; Prasad, G.; Singh, V.N. Treatment of carpet and metallic effluents by china clay. J. Chem. Technol. Biotechnol. **1992**, *55*, 277.
23. Kilinckale, F.; Ayhan, S.; Apak, R. Solidification-stabilization of heavy metals-loaded red muds and fly ashes. J. Chem. Technol. Biotechnol. **1997**, *69*, 240.
24. Ghosh, R.; Sinha, T.K.; Saxena, N.C. Bulk utilisation of fly ash. J. IAEM **2000**, *27*, 252.

Received February 2002
Revised July 2002