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ADSORPTIVE REMOVAL OF FIVE HEAVY METALS FROM WATER USING BLAST FURNACE SLAG AND FLY ASH

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ABSTRACT

Heavy metals can be serious pollutants of natural water bodies causing health risks to humans and aquatic organisms. A study was conducted to remove five heavy metals from water by adsorption onto an iron blast furnace slag and a fly ash in batch experiments. Increase of pH increased adsorption of all metals. Equilibrium adsorption of all metals was successfully modelled using Langmuir, Freundlich and Dubinin-Radushkevich models, with Freundlich model fitting the data the best. Langmuir adsorption maximum at pH 6.5 for fly ash ranged 3.4 - 5.1 mg/g with the adsorption capacity for the metals in the order, Pb > Cu > Cd, Zn, Cr. The corresponding values for furnace slag were 4.3 - 5.2 mg/g, and the order of adsorption capacities, Pb, Cu, Cd > Cr > Zn. The kinetics of adsorption fitted well to both the pseudo-first order and pseudo-second order models, but the fit was slightly better for the pseudo-second order model.

1. INTRODUCTION

Elevated concentrations of heavy metals in the environment can cause health risk to humans and aquatic organisms and therefore they should be removed from water. Various processes for the removal of heavy metals are available, of these, adsorption method is generally considered to be attractive because of its effectiveness, simplicity of operation, and environmental considerations, provided low-cost adsorbents are used.

Steel plants generate a large volume of granular blast furnace slag as a by product waste. This waste has been converted into an effective and economical scavenger and utilized for the remediation of aqueous Pb and Zn (Dimitrova and Mehandgiev 1998, Mishra and Patel 2009) and Cu, Ni, and Zn (Dimitrova 1996). Fly ash, an industrial solid waste of thermal power plants located in many countries, is another low-cost adsorbent having good removal capabilities for Pb and Cr (Gupta and Ali 2000) and Pb and Zn (Mishra and Patel 2009). However, limited studies have been conducted on the use of furnace slag and fly ash for the removal of several metals under common experimental conditions.

The aims of the present paper are to (i) study the feasibility of using blast furnace slag and fly ash as adsorbents for the removal of five different heavy metal ions from aqueous solutions, (ii) study the effect of initial pH on the adsorption process and (iii) model the equilibrium and kinetic adsorption data.

2. MATERIALS AND METHODS

2.1. Adsorbents

Blast furnace slag and fly ash were obtained from Australasian (iron and steel) Slag Association (ASA), and Ash Development Association of Australia Inc, respectively. The chemical compositions of these materials are presented in Figure 1 and Table 1.

Table 1. The chemical composition (%) of fly ash and furnace slag.

% content	MnO	Fe_2O_3	Al_2O_3	SiO_2	CaO	MgO	Cr_2O_7	Other
Furnace slag	3.29	28.83	0.18	22.33	32.73	10.00	0.20	2.44
Fly ash	-	1.26	25.90	56.04	2.20	0.94	-	13.66

The change in chemical compositions and surface of the modified furnace slag and fly ash before and after adsorption will be determined by XRD and SEM analysis methods (Nova Namo Scaning Electron Microscopy NEP 199).

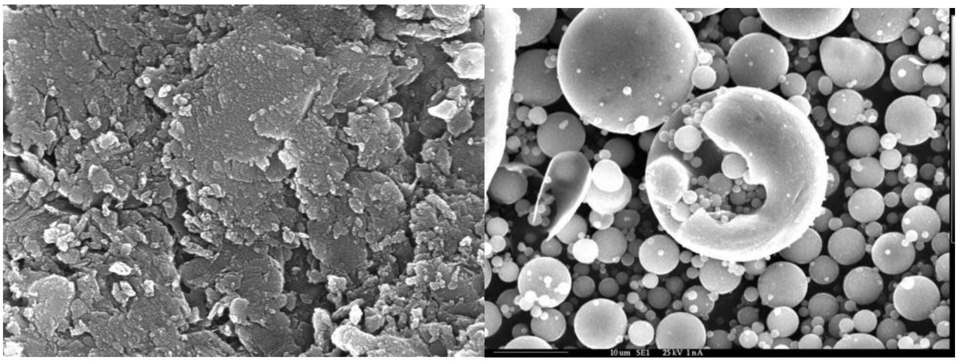

Figure 1. SEM images of furnace slag (left) and fly ash (right).

2.2. Zeta potential

Zeta potentials of the adsorbents were measured on 10 mL suspensions containing 1.0 g adsorbent at different pHs using a zeta sizer nano instrument (Nano ZS Zen3600, Malvern, UK) after shaking the suspensions for 8 hours.

2.3. Adsorption studies

Adsorption of heavy metals onto the adsorbents was studied in batch experiments by shaking 0.01 to 2.0 g of adsorbent with metals, each at an initial concentration of 5 mg/L, in 100 mL solutions at a pH of 6.5 and ionic strength of 10^{-3} M $NaNO_3$ at 25 ± 2 °C for 24 h and filtering the suspensions. The filtrates were analysed for heavy metals concentrations using a Microwave Plasma-Atomic Emission Spectrometer (MP-AES- 4100 Agilent) and amounts of metals adsorbed were determined. Similar experiments were conducted at pH ranging from 2 - 9 to determine the effect of pH on adsorption. Kinetics of adsorption were studied by shaking 100 mL nitrate solution of each metal at a concentration of 5 mg/L and 0.5 g adsorbent dose for different times (10 mins to 14 h) at an ionic strength of 10^{-3} M $NaNO_3$ and pH 6.5.

3. RESULTS AND DISCUSSION

3.1. Zeta potential

Fly ash is a heterogeneous material consisting largely of small spheres, formed by the condensation of aluminous and siliceous glass droplets in the air. BET surface area of fly ash was 2.82 m^2/g while that of furnace slag was 1.06 m^2/g.

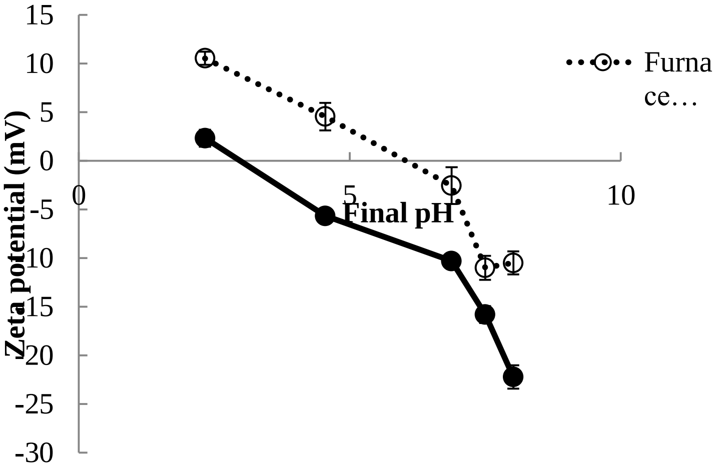

Figure 1. Zeta potential of fly ash and furnace.

Zeta potential values showed that the fly ash and furnace slag particles were positively charged at low pH's and negatively charged at high pH's (Fig. 2). The point of zero charge (PZC) of fly ash was at a pH of 3.0 and that of furnace slag was at a pH of 6.0. Therefore, it can be expected that positively charged metal ions are likely to adsorb by Coulombic forces (outer-sphere complexation) onto the negatively charged fly ash particles at pH above 3.0 and above pH 6.0 in furnace slag. However, adsorption by other forces (inner-sphere complexation) can occur at all pHs independent of the PZC. The high content of SiO_2 in fly ash (Table 1) might have resulted in the low PZC of fly ash. In comparison to fly ash, the furnace slag had a higher PZC, probably due to the high contents of Fe and Ca oxides. SiO_2 is known to have PZC of 3.6 (Hommer 2009), Fe_2O_3 of pH 7.9 (Nagata et al. 2009) and CaO 10.5 (Azgomi. 2014).

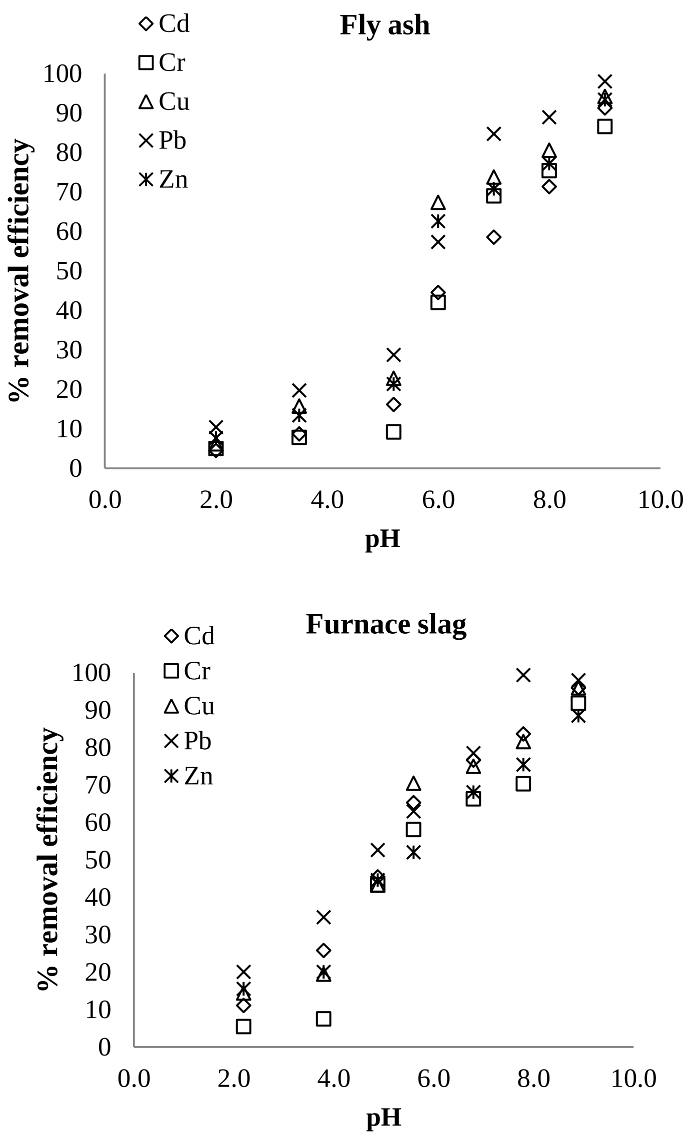

Figure 3. pH effect of fly ash and furnace slag of heavy metals.

Increase of pH increased metals adsorption. For fly ash, abrupt increase in adsorption of all metals occurred at pH 5.5 - 7.0, whereas for furnace slag, this occurred at pH 4.0 - 6.0 (Fig. 3). The lower pH range where abrupt increase in adsorption occurs for furnace stag cannot be due to increase in negative surface charges on the adsorbent because the pH at which negative charges start to increase was higher for furnace slag compared to fly ash. For fly ash, abrupt increase in adsorption of all metals occurred at pH 5.5 - 7.0, whereas for furnace slag, this occurred at pH 4.0 - 6.0 (Fig. 3).

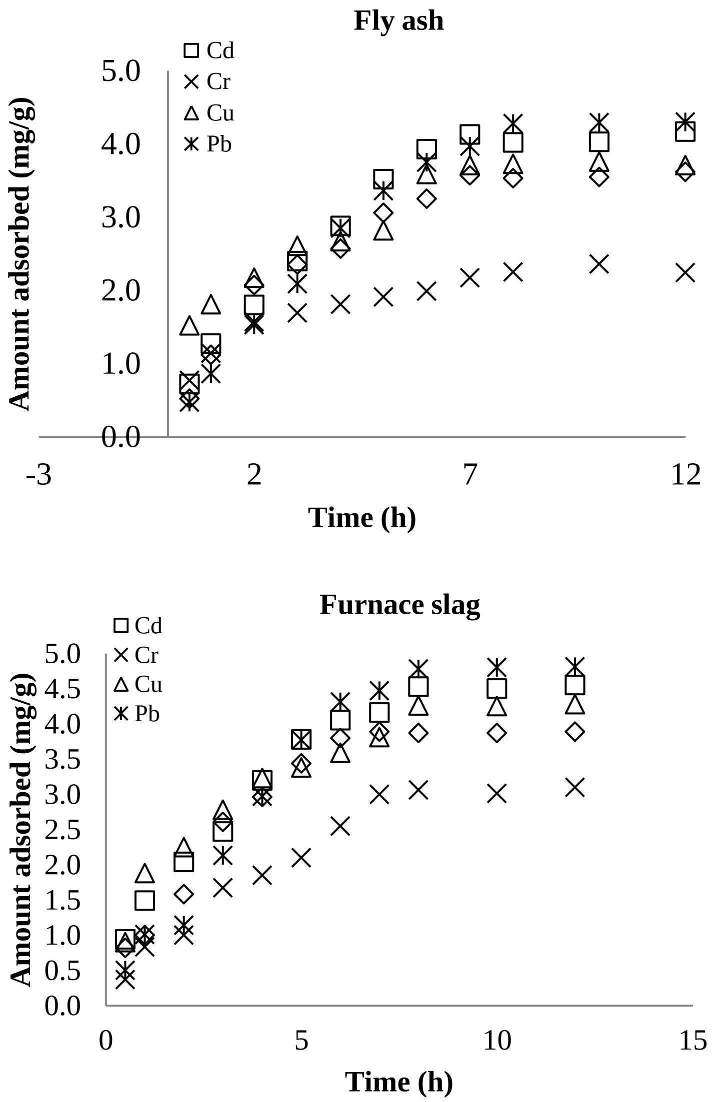

Figure 4. Kinetics of heavy metal adsorption.

Equilibrium adsorption of all metals at pH 6.5 was successfully described using Langmuir, Freundlich and Dubinin-Radushkevich models, with Freundlich model fitting the data the best (Table 2). Langmuir adsorption maximum at pH 6.5 for fly ash ranged 3.4 - 5.1 mg/g with the adsorption capacity for the metals in the order, Pb > Cu > Cd, Zn, Cr. The corresponding values for furnace slag were 4.3 - 5.2 mg/g, and the order of adsorption capacities, Pb, Cu, Cd > Cr > Zn. The kinetics of adsorption fitted well to both the pseudo-first order and pseudo-second order models, but the fit was slightly better for the pseudo-second order model.

Table 2. Langmuir adsorption isotherm parameters for heavy metals adsorption on fly ash and furnace slag.

	Metals	Langmuir			Freundlich			Dubinin–Radushkevick		
		qmax (mg/g)	K_L (L/mg)	R^2	n	K_F (L/mg)	R^2	q_m (mg/g)	β (mol^2/kJ^2)	R^2
FA	Cd	3.78	0.86	0.8906	1.86	1.44	0.9670	2.03	4×10^{-8}	0.8069
	Cr	3.53	0.73	0.9172	1.90	1.26	0.9754	1.63	3×10^{-8}	0.6871
	Cu	4.49	0.44	0.8843	1.60	1.19	0.9916	1.94	6×10^{-8}	0.7721
	Pb	5.11	0.42	0.9091	1.46	1.33	0.9804	2.32	7×10^{-8}	0.8349
	Zn	3.40	0.62	0.8714	1.67	1.13	0.9435	2.86	6×10^{-8}	0.5761
FS	Cd	5.05	0.44	0.7939	1.58	1.37	0.9549	1.92	4×10^{-8}	0.6766
	Cr	4.83	0.47	0.9023	1.51	1.33	0.9075	2.06	5×10^{-8}	0.7647
	Cu	5.22	0.68	0.9773	1.62	1.77	0.9890	2.62	5×10^{-8}	0.8670
	Pb	4.93	0.86	0.8999	1.80	1.83	0.9925	2.54	3×10^{-8}	0.8527
	Zn	4.26	0.78	0.8960	1.99	1.53	0.9806	1.92	2×10^{-8}	0.6922

qmax: maximum adsorption capacity (mg/g); K_L = Langmuir constants; qe = the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g); K_F and n = Freundlich constants; q_m = the monolayer capacity, and β = activity coefficient.

Table 3. Pseudo-first order and pseudo-second order kinetic models parameters for the adsorption of heavy metals on fly ash and furnace slag.

	Metals	q_e exp (mg/g)	Pseudo-first-order			Pseudo-second-order		
			q_e (mg/g)	$k_1 \times 10^{-2}$	R^2	q_e (mg/g)	$k_2 \times 10^{-2}$	R^2
FA	Cd	4.10	2.90	0.34	0.8419	1.76	-	0.9851
	Cr	2.25	1.43	0.14	0.8241	1.06	-	0.9803
	Cu	3.71	3.86	0.31	0.8914	2.07	1.07	0.9844
	Pb	4.30	4.81	0.28	0.9443	2.34	0.31	0.9828
	Zn	3.62	3.02	0.24	0.9138	1.79	1.53	0.9760
FS	Cd	4.55	7.12	0.52	0.9226	5.96	0.05	0.9795
	Cr	3.10	4.79	0.44	0.9091	4.92	0.08	0.9288
	Cu	4.28	5.66	0.46	0.9008	5.18	0.08	0.9918
	Pb	4.81	11.14	0.58	0.9379	9.72	0.01	0.7315
	Zn	3.89	3.41	0.35	0.8672	5.28	0.06	0.9549

qe = amount of heavy metals adsorbed at equilibrium (mg/g); k_1 = equilibrium rate constant of pseudo-first-order sorption (1/min); k_2 = equilibrium rate constant of pseudo-second-order sorption (1/min); R^2: coefficient of determination

4. CONCLUSIONS

The study showed that the industrial by-products, fly ash and blast furnace slag are effective low-cost adsorbents for the removal of Pb, Cu, Cd, Cr, and Zn from water. The effectiveness of adsorption increases with increase in pH, reaching maximum adsorption at pH 6-7. Equilibrium adsorption at pH 6.5 was best explained by Freundlich model and kinetics of adsorption by pseudo-second order model (Table 3).

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