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. The purpose of this study was to investigate the removal of five heavy metals from water by adsorption onto: an iron industry blast furnace slag waste (point of zero charge (PZC) pH 6.0; main constituents, Ca and Fe); and a coal industry fly ash waste (PZC 3.0; main constituents, Si and Al). Batch study revealed that rising pH increased the adsorption of all metals with an abrupt increase at pH 4.0-7.0. The Langmuir adsorption maximum for fly ash at pH 6.5 was 3.4-5.1 mg/g with the adsorption capacity for the metals being in the order, Pb > Cu > Cd, Zn, Cr. The corresponding values for furnace slag were 4.3 to 5.2 mg/g, and the

order of adsorption capacities was Pb, Cu, Cd > Cr > Zn. Fixed-bed column study on furnace slag/sand mixture (1:1 w/w) revealed that the adsorption capacities were generally less in the mixed metals system (1.1 – 2.1 mg/g) than in the single metal system (3.4-3.5 mg/g). The data for both systems fitted well to the Thomas model, with the adsorption capacity being highest for Pb and Cu in the single metal system and Pb and Cd in the mixed metals system. Our study showed that fly ash and blast furnace slag are effective low-cost adsorbents for the simultaneous removal of Pb, Cu, Cd, Cr, and Zn from water.

Introduction

Elevated concentrations of heavy metals in water pose a serious health risk to humans and aquatic life forms (Ahmaruzzaman 2011; Fu and Wang 2011; Saha et al. 2011). Consequently, regulatory agencies have set maximum permissible limits for the discharge of heavy metals into aquatic systems. Therefore, the removal of these metals from contaminated water is important for the protection of human health and the environment. Precipitation/coagulation is a widely-used method to remove heavy metals. But this process commonly generates large amounts of low density fluffy sludge which generates dewatering and disposal problems. Furthermore, it is not effective in removing heavy metals that occur at low concentrations (Fu and Wang 2011). Membrane filtration is an effective means of metal ions removal but its high cost is a disadvantage. The adsorption method is generally considered to be attractive because of its high effectiveness, simplicity and flexibility of plant design and operation, and environmental

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considerations (Fu and Wang 2011). Another advantage is that the adsorption process is generally reversible, and therefore, the adsorbent can be regenerated by desorption of the adsorbed metals for multiple reuse (Nguyen et al. 2015).

One of the economic means of removing heavy metals using the adsorption process is using low-cost adsorbents. Several review papers have summarised the adsorption capacities of heavy metals in low-cost adsorbents (Ahmaruzzaman 2011; Bailey et al. 1999; Gupta and Ali 2000; Kurniawan et al. 2006; Saha and Orvig 2010; Wang et al. 2003). Of these low-cost adsorbents, industrial by-products are useful materials for the removal of heavy metals, not only because of their low cost but also using this process to some degree solves the problem of environmental pollution arising from disposal of this by-product waste.

Fly ash is a coal industry by-product and has been used as an economical adsorbent for removing heavy metals. The generation of coal combustion products of which fly ash is an important component amounted to 780 million tonnes in 2010 (Heidrich et al. 2013). The use of fly ash for removing heavy metals from industrial wastewaters was reported many decades ago (Gangoli et al. 1975; Grover and Narayanaswamy 1982). Bayat (2002) reported that the higher the Ca content in the fly ash the greater the adsorption capacity of heavy metals. Apak et al. (1998) studied single metal and mixed metals (competitive adsorption) adsorption of Pb, Cu and Cd by fly ash and reported that the adsorption affinity of the metals in both the single and mixed metals systems followed the order Cu > Pb > Cd. They explained this as being due to energetic reasons in which the hydrolysis products and hydroxide precipitates of the metals adsorb with higher affinity. A similar reasoning was given for the following order of removal of heavy metals by a South African fly ash: Pb > Cr > Cu > Ni > Zn > > Cd (Ricou et al. 1998).

Steel plants generate a large amounts of blast furnace slag as a by-product, causing a serious disposal problem. World steel slag production amounted to about 170-250 million tonnes in 2013 (van Oss 2014). Blast furnace slag has high adsorption capacity for heavy metals

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because of the presence of Al and Fe oxides in them (Dimitrova and Mehandgiev 1998; Gupta 1998). Dimitrova (1996) studied the adsorption of Cu, Ni and Zn from simulated wastewater using blast furnace slag in a batch study and found that the Freundlich adsorption constant related to the adsorption capacity was in the order, Cu > Zn > Ni. They explained that the adsorption capacities were linked to: firstly, the tendency of metals adsorbing as hydroxide complexes; and secondly, the formation of insoluble compounds on the internal surface of adsorbent. In a subsequent column adsorption study, it emerged that a granulated blast furnace slag had column breakthrough adsorption capacities following the sequence, Pb > Cu > Cd > Ni (Dimitrova, 2002).

Competitive adsorption of metals is of primary importance in water and wastewater treatment because most metal ions coexist with each other in solution. However, only a few studies investigated the simultaneous adsorption of mixed heavy metals on coal fly ash and furnace slag. These studies have mainly been done on the static batch system. Column studies which are dynamic and closer to the operational conditions in treatment plants are necessary.

The aims of this paper were to: (i) study the feasibility of using blast furnace slag and coal fly ash as adsorbents for removing five heavy metal ions (Cd, Cr, Cu, Pb, and Zn) from aqueous solutions in single metal and multi-metals systems in batch and column adsorption experiments; (ii) investigate the influence of pH on adsorption; and (iii) model the adsorption data.

Materials and methods

Adsorbents characterisation

Fly ash and blast furnace slag samples were obtained from Coal Ash Development

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Association of Australia Inc. and Australasian (iron and steel) Slag Association (ASA), respectively. Furnace slag used in this study was produced by BlueScope Steel in Port Kembla, NSW, Australia, and this slag constitutes an abundant by-product in the steel manufacturing process. The furnace slag was treated with H_2O_2 at 60 °C for 24 h to oxidise the organic matter in the slag. It was subsequently washed with de-ionised water, dried at 100 °C, powdered, and then sieved to 150 - 300 µm. This size fraction was used for the study. As received fly ash of particle size 10-20 µm was used for the study.

Zeta potentials of the adsorbents were measured in 10 mL suspensions containing 1.0 g adsorbent at different pHs after shaking the suspensions for 8 hours. Zeta potential was measured using a Zetasizer nano instrument (Nano ZS Zen3600, Malvern, UK) after measuring the final pH. Surface area was determined by BET nitrogen-sorption measurements using a Micromeritics 3 Flex surface characterisation analyser. A XRD Shimadzu S6000 (Japan) diffractometer equipped with a Cu target was used to determine the mineralogy on powder samples of the adsorbents. The diffractometer was operated at 40 kV and 30 mA with a setting of $5 - 45^\circ$ (2θ), at increasing step rate of 2°/min.

Batch experiments

Adsorption of heavy metals onto the adsorbents was studied in batch experiments by shaking 0.01 to 2.0 g of adsorbents 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. The pH was kept constant at 6.5 by adding 0.01 M NaOH during the first 4 h when the pH decreased. Thereafter, there was no change in pH till the end of the experiment. Past studies also showed decrease of pH during heavy metals adsorption (Sounthararajah et al. 2015; Su et al. 2010). The suspensions were filtered and the heavy metal concentrations in the filtrate were analysed using

a Microwave Plasma-Atomic Emission Spectrometer (MP-AES-4100 Agilent). The amounts of metals adsorbed were determined by subtracting the amounts of metals in the filtrate from the amounts of the respective metals initially added. The adsorption data were fitted to the Langmuir, Freundlich and Dubinin–Radushkevick adsorption isotherms (Sounthararajah et al. 2015).

To study the influence of pH on metal ion adsorption, the pH of the metal ion solution (5 mg/L in 100 mL) was changed (pH 2-9) by adding dilute NaOH or HCl solution. 0.5 g of adsorbent was added to the pH adjusted solution and the suspensions were agitated in a flat shaker at a shaking speed of 120 rpm for 12 h at room temperature (25 ± 2 ^{o}C). The pH was kept constant at the initial value by adding 0.01 M NaOH or 0.01 M HCl during the first 4 h when the pH changed. Thereafter, there was no change in each pH study till the end of the experiment. The amounts of metals adsorbed were determined as described previously.

Column experiments

The fixed-bed column used for the experiments consisted of 2.0 cm inner diameter Pyrex glass tubes. Column adsorption experiments were conducted by passing solutions of Zn, Cu, Cd, and Pb at concentrations of 5 mg/L of each metal through the column containing 80 g of furnace slag and 80 g of sand mixed together and packed to a height of 12 cm. Column experiment was not conducted on fly ash because it was not possible to pack fly ash in the column and maintain a constant flow of solution through the column. The fly ash formed a cake and blocked the water flow.

Distilled water adjusted to an ionic strength of 10^{-3} M NaNO$_3$ was used in the batch adsorption experiments. Because large quantities of distilled water were not freely available for the continual dynamic operation in column study, tap water (ionic strength 95 mg/L) was used

in the column experiments. Heavy metals were added separately to tap water to produce a concentration of 5 mg/L each metal, and each metal solution was filtered downwards through the column at a flow rate of 20 mL/min (1.0 m/h). Two peristaltic pumps; one at the inlet of the solution and the other at the outlet were used to maintain the flow rate. Filtrates were periodically collected at regular intervals and analysed for pH and heavy metals concentrations. A similar experiment was conducted with a mixture of heavy metals with each metal at the same concentration as in the single metals experiment. The column adsorption capacity, q_{total} (mg) was calculated by computing the area within the plot of the adsorbed metal concentration, C_{ad} ($C_{ad} = C_o - C$) (mg/L) against time (t, min) (C_o is feed heavy metal concentration, C is effluent heavy metal concentration). A Microsoft Excel spread sheet was used for the calculation which was based on Equation (1), where Q is the velocity of the solution (L/min):

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=60} C_{ad}\, dt \qquad (1)$$

The breakthrough data was simulated using Thomas model (Thomas 1944). The model was derived from the equation of mass conversation in a flow system. It had the assumption that the rate of the driving force obeys second order reversible reaction kinetics and the adsorption equilibrium follows the Langmuir model with negligible axial and radial dispersion in the fixed-bed column.

The main rationale of using this adsorbent was its low cost, produced from an ample supply of waste material. Therefore, it was not regenerated for repeated use as in the case of other adsorbents (Nguyen et al. 2015; Sounthararajah et al. 2015) for economic reasons.

Results and discussion

Characterisation of fly ash and furnace slag

The chemical compositions of these materials are presented in Table 1. The fly ash was composed mainly of SiO_2 and Al_2O_3 whereas the furnace slag consisted mainly of CaO and Fe_2O_3. These compositions agree with those reported for fly ash by Cho et al. (2005) and for blast furnace slag microspheres by Lee et al. (2012). BET surface area of fly ash was 2.82 m^2/g while that of furnace slag was 1.06 m^2/g.

The XRD pattern of the fly ash sample indicated that the sample consisted mainly of quartz and mullite minerals (Figure 1). Koukouzas et al. (2006) have reported that these two minerals were the dominant constituents of a Chinese fly ash based on their XRD analysis. The XRD pattern of the furnace slag indicated that the slag consisted of many minerals of which gehlenite, wollastonite, and merwinite were the predominant ones, as observed in a South African blast furnace slag (Lewis 1982).

Zeta potential values showed that the fly ash and furnace slag particles were positively charged at low pHs and negatively charged at high pHs (Figure 2). The point of zero charge (PZC, the pH at which the net surface charge is zero) of fly ash was at a pH of 3.0 while that of furnace slag was at a pH of 6.0. It can therefore be expected that positively charged metal ions are likely to be adsorbed by Coulombic forces (outer-sphere complexation; Loganathan et al. 2014) 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; Loganathan et al. 2014) can also occur at all pHs independent of the PZC. The high content of SiO_2 in fly ash (Table 1) may 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 a

PZC of 2.0-3.7 (Park 1965), Fe_2O_3 of 5.5-9.0 (Park 1965) and CaO of 11.8 (Oladoja et al. 2012). The PZC of fly ash of pH 3 is closer to the value of pH 2.8 reported for a coal fly ash from Korea (Cho et al. 2005). The PZC of blast furnace slag of pH 6.0 is not very different from the value of 7.6 reported for blast furnace slag microspheres by Lee et al. (2012).

Effect of pH on adsorption

The increase in pH subsequently increased metals adsorption. For fly ash, an abrupt increase in adsorption of all metals occurred at pH 5.5-7.0, whereas for furnace slag this occurred at a lower pH of 4.0-6.0 (Figures 3). The lower pH range where abrupt increase in adsorption occurs for furnace stag cannot be due to an increase in negative surface charges (zeta potentials) on the adsorbent. This is because the pH at which negative charges start to increase was higher for furnace slag compared to fly ash (Figure 2). There is practically no removal of metals at pH lower than 3.0 which may be due to the presence of a high concentration of H^+ at low pH that competed with the metals for adsorption and fewer negative surface charges on the adsorbents. The abrupt increase in adsorption at pH 4.0-7.0 is due to the formation of metal hydroxide precipitation on the surface of the adsorbents and adsorption of metal hydroxide complex (MOH^+) whose concentration increases at pH 5.0-7.0 depending on the metal (Southararajah et al. 2015). Metal hydroxide complexes have higher affinity to the adsorbent surface than simple divalent metal ions (Loganathan et al. 2012).

The pH of precipitation is governed by the solubility product of the metal hydroxide (pK_{so}) and pH of metal hydroxide complex formation is determined by the first hydrolysis constant (pK_1) (Table 2). The higher the pK_{so} value, the lower is the pH of metal hydroxide precipitation on the adsorbent surface (Loganathan et al. 2012). Chromium hydroxide which has the lowest pK_{so} value (Table 2) precipitates at higher pH and therefore the abrupt increase

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in adsorption occured at a higher pH than other metals. An opposite trend was found for Pb which has the highest pK_{so} value. Also, not considering Cr, Pb has the lowest pK_1 value, and therefore the pH at which the metal hydroxide complex ($Pb(OH)^+$) started to form was lower than that of other metals resulting in abrupt increae in Pb adsorption at the lowest pH. Despite Cr having the lowest pK_1, it did not have a marked increase in adsorption at low pH because the trivalent Cr undergoes hydrolysis forming a complexity of ions and its behaviour cannot be explained by the value of pK_1 (Ragai et al. 1991).

Batch equilibrium adsorption

Equilibrium adsorption of all metals at pH 6.5 was successfully described using the Langmuir and Freundlich models, but poorly when the Dubinin-Radushkevich model was employed (Table 3). The Freundlich model fitted the data slightly better than the Langmuir model. The Langmuir maximum adsorption capacities for the metals followed the order, Pb > Cu > Cd, Zn and Cr. Despite furnace slag having a higher PZC than fly ash the adsorption capacities for the metals were generally higher for furnace slag (4.3 – 5.2 mg/g) than for fly ash (3.4 – 5.1 mg/g). This shows that electrostatic adsorption (outer-sphere complexation) was not the main mechanism of adsorption. Specific adsorption (inner-sphere complexation) of both the divalent metal ions and metal hydroxide complexes is probably the main mechanism. Also, despite the surface area of fly ash being larger than that of furnace slag, the adsorption capacities were lower for fly ash. Therefore, rather than total surface available for adsorption, the number of active sites available for adsorption is important. Furnace slag had higher adsorption capacities because it contained more iron oxide which specifically adsorbs heavy metals (Nguyen et al. 2015). The adsorption capacities of both fly ash and furnace slag are lower than that of many other adsorbents (e.g. zeolite, Nguyen et al. 2015; nanotitanate, Sounthararajah et al. 2015), but

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because these materials are wastes, they are cost effective and consequently suitable to be utilised as adsorbents.

Column adsorption on furnace slag

To investigate the adsorptive removal capacities of furnace slag column, heavy metal solutions with 5 mg/L initial concentration were treated in a column containing furnace slag mixed with clean sand. Results showed that the breakthrough curves of metals were closer to each other in single metal system than in the mixed metals system (Figures 4 and 5). In the mixed metals system, furnace slag appeared to be better in removing Pb and Cd than other metals whereas Pb and Cu were more efficiently removed in the single metal system. This was also observed in one study using Pb, Cd, Cu, Zn, and Cr adsorption on zeolite and iron-coated zeolite (Nguyen et al. 2015).

The influent pH to the column was maintained constant at 6.0 and 5.0 for single and mixed metals systems, respectively. The effluent pHs were approximately the same as the respective influent pHs for the single (6.0 ± 0.1) and mixed metals (5.0 ± 0.1) systems. One of the reasons for pH not changing in the effluent could be due to the short residence time the influent took to pass through the column. In the present trial, it was 7.2 min (slag + sand column depth was only 12 cm, filtration velocity 1 m/h). Another reason is that the slag was thoroughly washed with water and treated with H_2O_2 prior to the column study. Dimitrova (2002) also reported that when slag was acid washed to pH 5.5 prior to Pb adsorption the pH of the effluent remained the same at pH 5.5.

The Thomas model satisfactorily simulated the breakthrough curves obtained for single as well as mixed metals systems (R^2 = 0.86-1.00) (Table 4). The experimental breakthrough curves and Thomas model simulation fits to the data are shown in Figs. 4 and 5. The values

obtained for adsorption capacities (q_o) from the models are approximately equal to those calculated from the breakthrough curves (q_e). Both the model and breakthrough values were higher for each metal in the single metal system than in the mixed metals system. This is due to the competitive adsorption behaviour of the metals in the mixed metals system. Another reason is that adsorption in single metal system was conducted at a higher pH (pH 6) than in the mixed metals system (pH 5). Metals adsorption capacities are higher at higher pHs (Fig. 3). Lower adsorption capacities for metals in this system compared to the single metals system were also reported for heavy metals adsorption on other adsorbents (Nguyen et al. 2015; Southararajah et al. 2015). The column adsorption capacities were slightly lower than the respective Langmuir adsorption capacities obtained from the batch study for furnace slag (Table 3). Nguyen et al. (2015) also reported lower column values than batch values for heavy metals adsorption on zeolite and iron-coated zeolite. They offered two reasons for this: firstly, adsorption did not attain equilibrium in the column study in contrast to that in the batch study; and secondly, the column adsorption was calculated at a lower metal concentrations in the feed solution compared to higher metal concentrations in the batch study at which Langmuir adsorption maxima were calculated.

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 increased with pH, reaching maximum adsorption at pH 6-7. Equilibrium adsorption of all metals at pH 6.5 can be successfully modelled using the Langmuir, Freundlich and Dubinin-Radushkevich models, of which the Freundlich model fitted the data the best. The adsorption capacity for the metals for fly ash was in the order: Pb, Cu > Cd, Zn, Cr, whereas

for furnace slag it was Pb, Cu, Cd > Cr, Zn.

The column study on furnace slag revealed that the metals' adsorption capacities were generally less in the mixed metals system than in the single metals system, probably due to competitive adsorption of metals in the mixed metals system. The column adsorption data for both the single metal system and mixed metals system fitted well to the Thomas model. This model's prediction of adsorption capacity in the single metal system was highest for Pb and Cu in the single metal system and Pb and Cd in the mixed metals system.

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Figure 5. Breakthrough curves (solid circle) and Thomas model (solid line) simulation for heavy metals adsorption in furnace slag + sand column in the mixed metals system at influent pH 5.0. Effluent pH also shown (open circle).

Table 1. The chemical composition (%) of fly ash and furnace slag (Data provided by the Suppliers)

	MnO	Fe_2O_3	Al_2O_3	SiO_2	CaO	MgO	Cr_2O_3	Other
Fly ash	-	1.26	25.90	56.04	2.20	0.94	-	13.66
Furnace slag	3.29	28.83	0.18	22.33	32.73	10.00	0.20	2.44

Table 2. Metal hydroxides solubility products and first hydrolysis constants

Metal	Solubility product of metal hydroxides (pK$_{so}$)	First hydrolysis constant (pK$_1$)	Reference
Zn	16.5	8.96	Walker et al. (2012)
Cu	19.3	7.96	Rao (2011)
Cd	14.4	10.08	Barnum (1983)
Pb	19.9	7.71	Baes and Mesmer (1976)
Cr	12.4[*]	4.01[**]	[*]Lopez-Gonzalez et al. (2010)
			[**]Ragai et al. (1991)

Table 3. Adsorption isotherm parameters for heavy metals adsorption on fly ash (FA) and furnace slag (FS)

	Metals	Langmuir			Freundlich			Dubinin–Radushkevick		
		q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F (mg/g) (L/mg)$^{1/n}$	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

q_{max}: maximum amount of the adsorbate (heavy metal) per unit weight of the adsorbent (mg/g);

K_L: Langmuir constants; K_F (related to the adsorption capacity) and n: Freundlich constants;

q_m: the monolayer adsorption capacity; β: activity coefficient; R^2: coefficient of determination

Table 4. Breakthrough adsorption capacities and Thomas model parameters (Nguyen et al. 2015) for furnace slag column adsorption of heavy metals (HM) from single (pH 6.0) and mixed metals solution (pH 5.0)

HM	Individual metal				Metals mixture			
	Breakthrough adsorption capacity q_e (mg/g)	q_o (mg/g)	k_{Th} (mL/min.mg)	R^2	Breakthrough adsorption capacity q_e (mg/g)	q_o (mg/g)	k_{Th} (mL/min.mg)	R^2
Pb	4.05	3.52	1.54	0.9761	2.31	2.12	0.62	0.9587
Cd	3.68	3.47	1.56	0.9508	2.16	1.94	0.76	0.8613
Cu	4.11	3.47	1.54	0.9063	1.67	1.17	0.94	0.9118
Zn	3.73	3.46	1.60	0.9058	1.86	1.07	1.08	0.9955
Cr	3.55	3.43	2.08	0.9413	1.62	1.39	0.82	0.9572

q_e: breakthrough adsorption capacity (mg/g),

q_o: Thomas adsorption capacity (mg/g), K_{Th}: Thomas rate constant (mL/min.mg)

(a)

Quartz - SiO2   Mullite - synthetic - Al6Si2O13

Gehlenite - Al2O3·3CaO·2SiO2   Iscorite, syn - Fe7(SiO4)O6

Wollastonite - CaSiO3   Calcium Iron Oxide - Ca0.15Fe2.85O4

Merwinite - Ca3Mg(SiO4)2   Hatrurite, syn - Ca3SiO5

(b)   Merwinite, syn - Ca3Mg(SiO4)2   Enstatite ferroan - (Mg1.014Fe.986)Si2O6
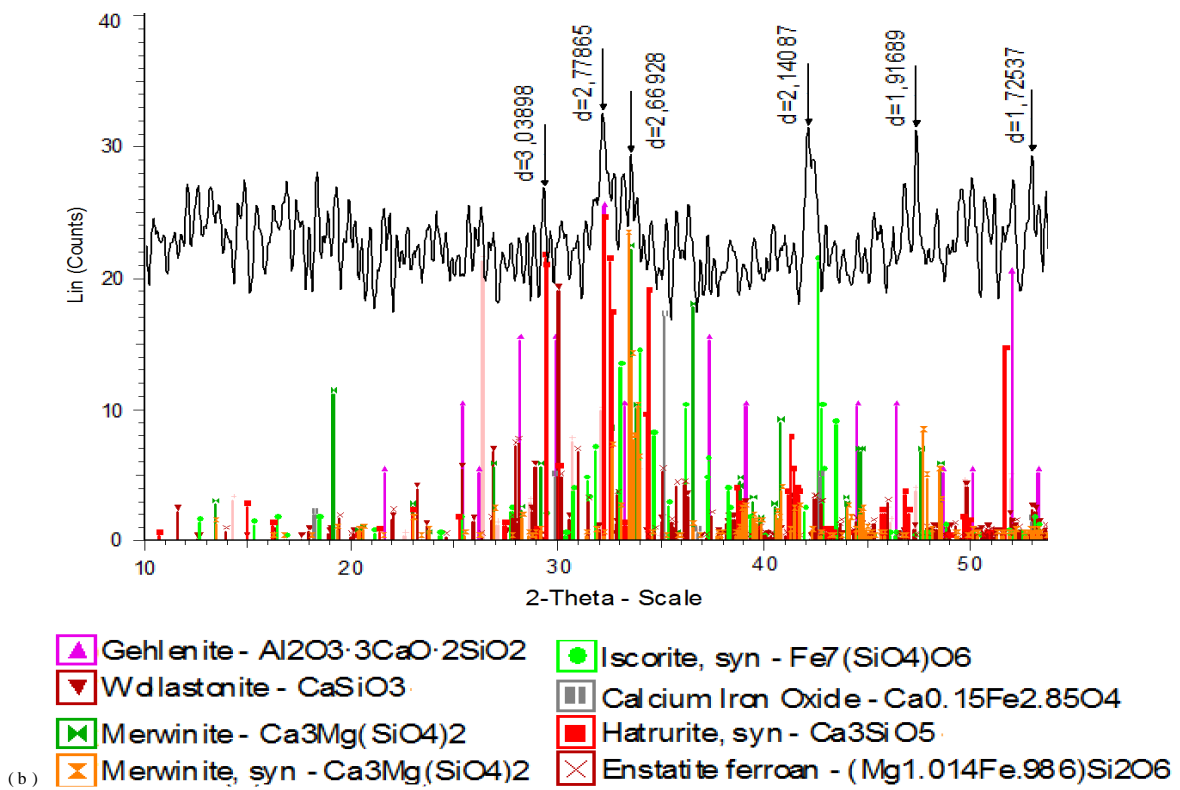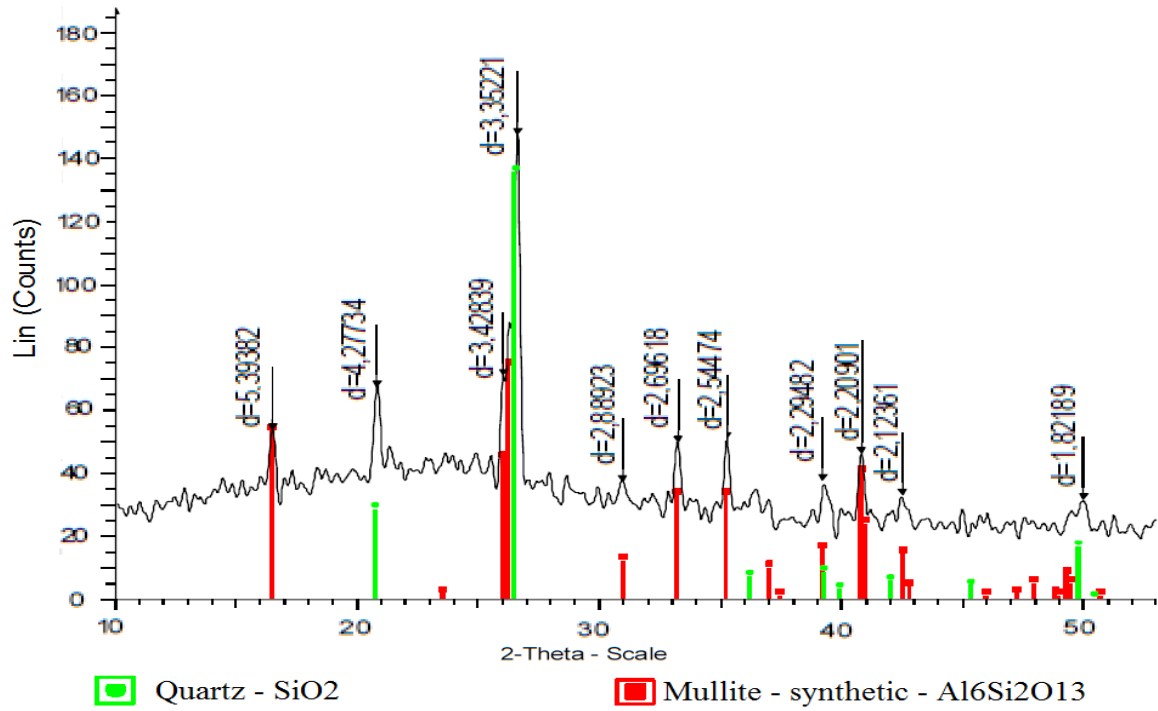
Figure 1. XRD patterns of (a) fly ash and (b) furnace slag

Figure 2. Zeta potential of furnace slag and fly ash

C d **(a) F A** C r

C u   P b

Z n

%Efficiency

0 . 0   2 . 0   4 . 0   6 . 0   8 . 0   1 0 . 0

p H

0   **(b) F S**

0 . 0   2 . 0   4 . 0   6 . 0   8 . 0   1 0 . 0
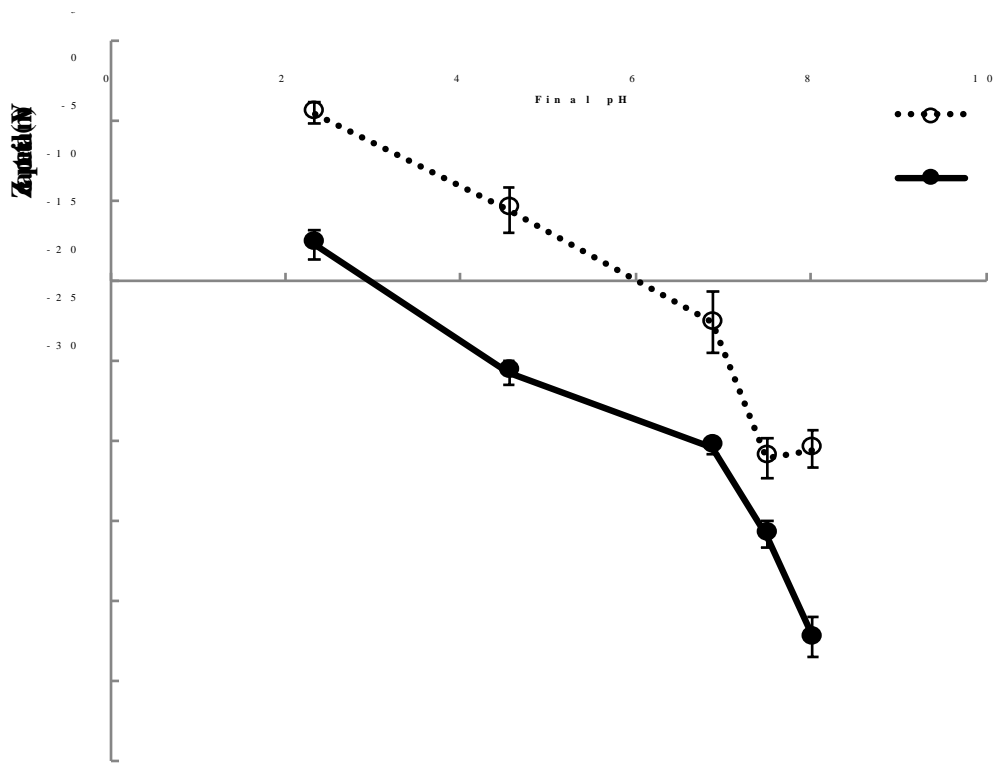
p H
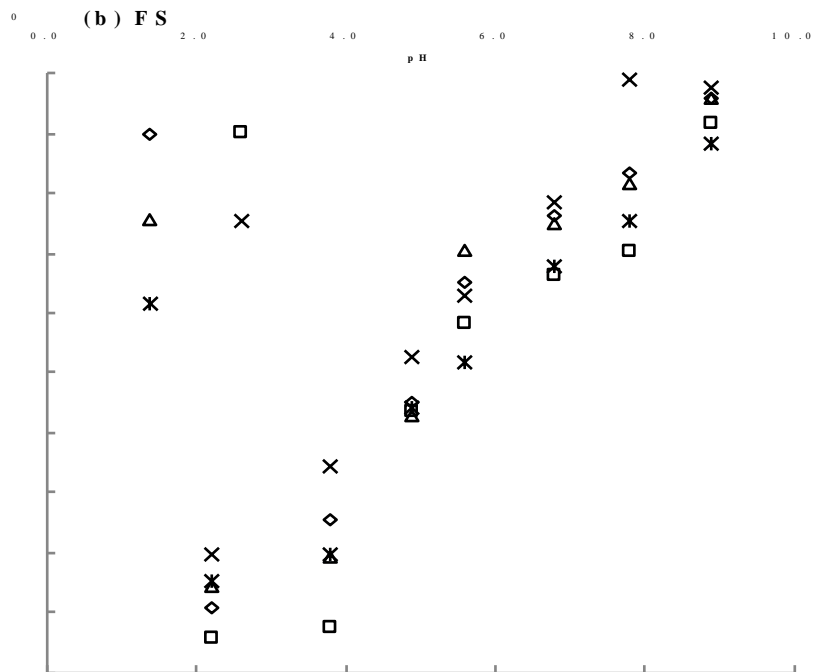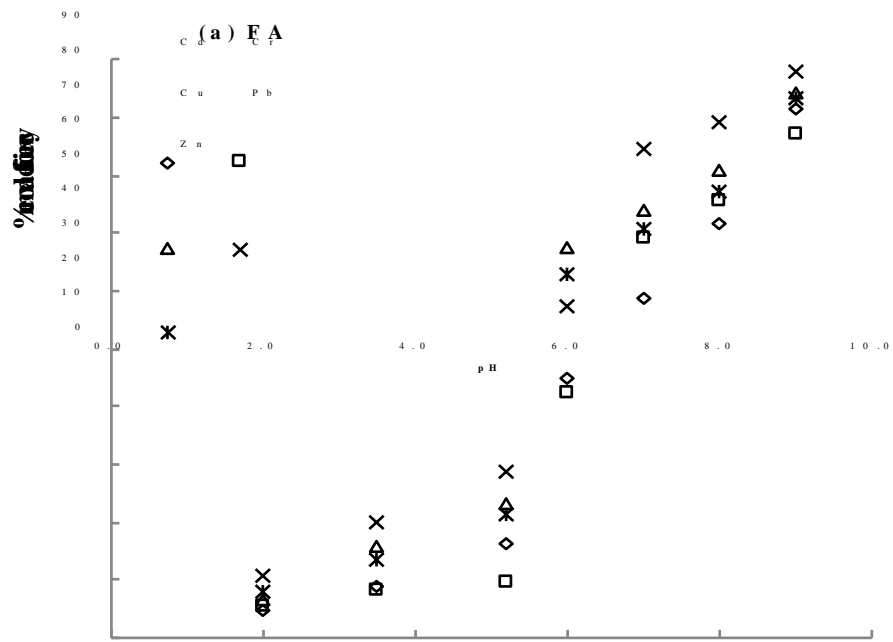
F i g u r e 1 . E f f e c t o f p H o n t h e a d s o r p t i o n o f h e a v y m e t a l s b y (a) f l y a s h (F A) a n d (b)

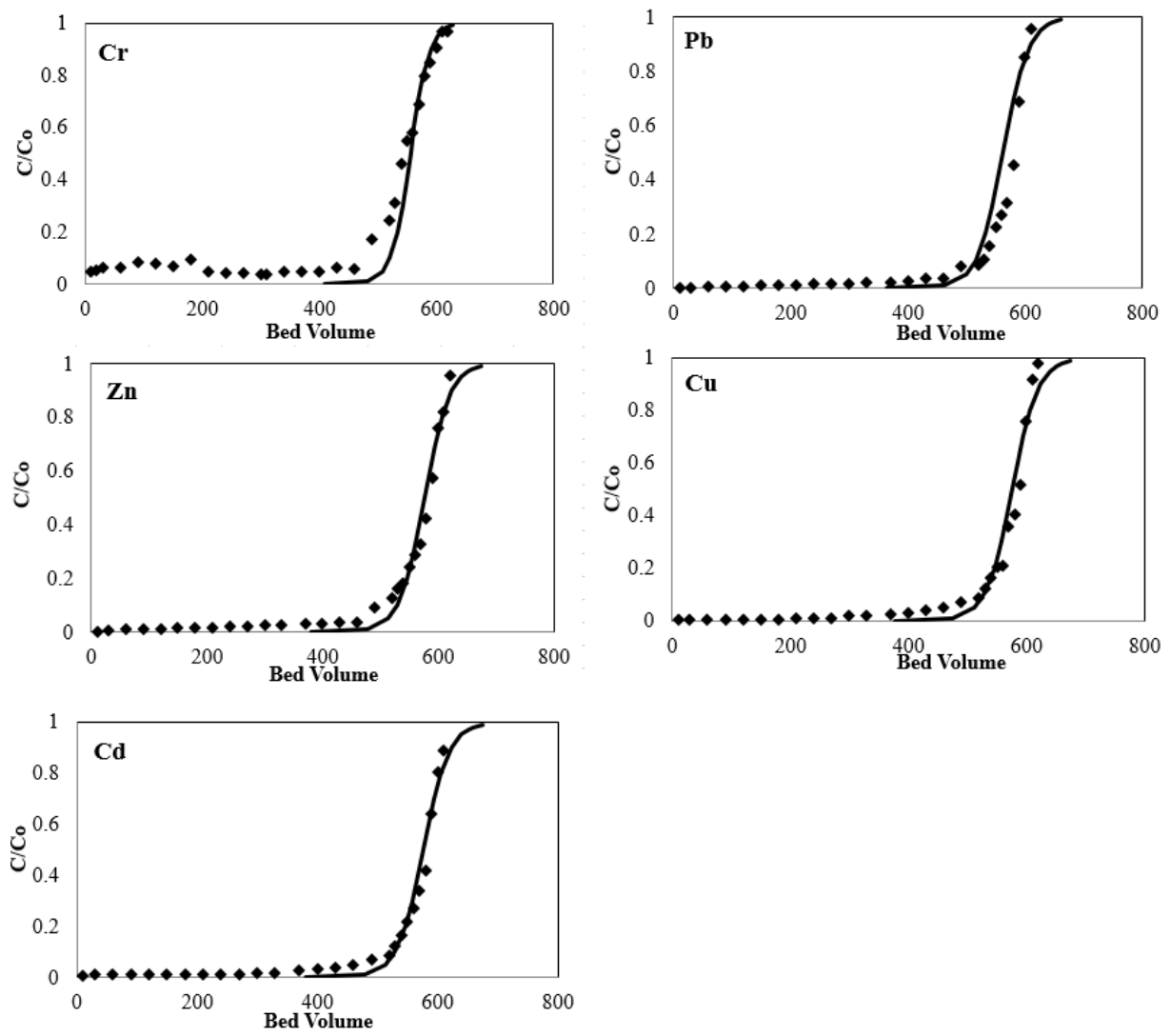f u r n a c e s l a g (F S)

Figure 4. Breakthrough curves (solid circle) and Thomas model (solid line) simulation for heavy metals adsorption in furnace slag + sand column in the single metal system at influent pH 6.0. Effluent pH also shown (open circle).
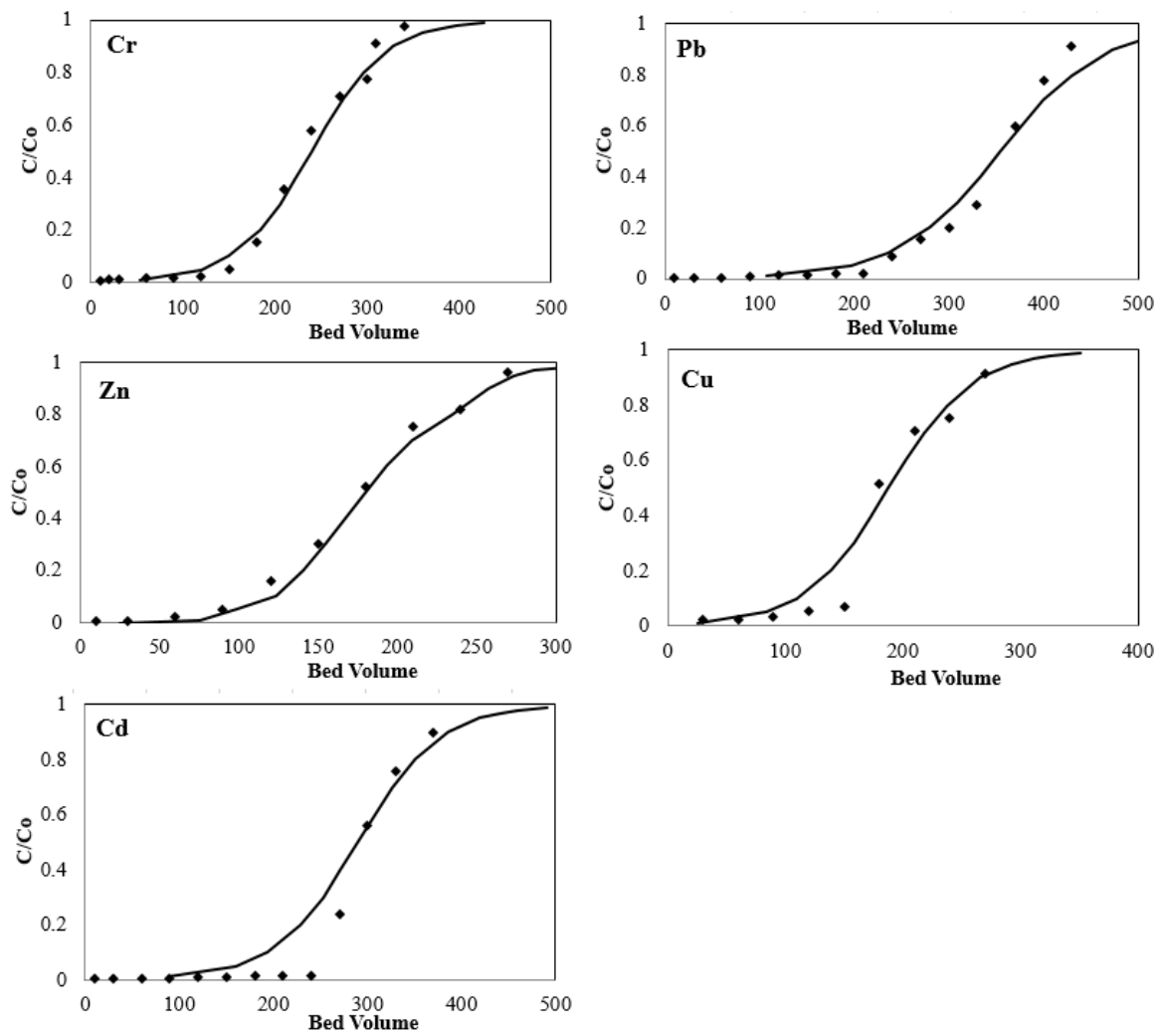
Figure 5. Breakthrough curves (solid circle) and Thomas model (solid line) simulation for heavy metals adsorption in furnace slag + sand column in the mixed metals system at influent pH 5.0. Effluent pH also shown (open circle).