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ORIGINAL ARTICLE

Evaluation of the use of an alkali modified fly ash as a potential adsorbent for the removal of metals from acid mine drainage

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Abstract The coal fly ash (FA), mainly containing high unburnt carbon was modified by alkali hydrothermal treatment. The modified fly ash (MFA) contains lower amounts of Si and Al and has a higher surface area and pH than the untreated fly ash (FA). The objective of this study is to investigate the potential of MFA as a low cost adsorbent material for the removal of Al, Fe, Ni, Pb, Zn and Mn from acid mine drainage (AMD). The effect of dose, contact time and competing cations on the adsorption of metals was investigated. The results showed that the sorption process onto MFA was initially rapid, but slowed down thereafter. The optimum time for metal uptake was 180 min while the optimum dose of MFA for metal removal was 120 g/L. The adsorption data best fit to the Freundlich isotherm model, which demonstrates that the adsorption process is controlled by the heterogeneous nature of the adsorbent. Adsorption kinetics of Al, Fe, Ni, Pb, and Zn onto MFA follow a pseudo second-order reaction, which implies that chemisorption is the

adsorption rate-limiting step for them, while for Mn it is intra-particle diffusion. Preliminary treatment of real mine drainage from Jaintia Hills coalfield indicates that MFA can be an effective and low-cost adsorbent for the treatment of AMD. The desorption data show that most of the metal ions were substantially desorbed in the acidic media, implying that the adsorbent can be regenerated and reused efficiently.

Keywords Modified coal fly ash · Acid mine drainage · Adsorption · Heavy metals

Introduction

Acid mine drainage (AMD) resulting from the oxidation of sulfide minerals causes severe environmental pollution of natural watercourses and in turn poses threats to human health (Akcil and Koldas 2006) because of its high concentrations of heavy metals, which are non-biodegradable and non-biocompatible; thus they tend to accumulate in living organisms that leads to various kinds of diseases (Alvarez-Ayuso et al. 2003; Sprynskyy et al. 2006). Generation of AMD around working as well as abandoned multimetal sulfide ore bodies and working coal mines of Tertiary ages is quite extensive throughout the world. Therefore, removal of metals from AMD has become a high priority research area. There are several techniques that have been developed for treatment of AMD, including precipitation, electro-dialysis, ultra-filtration, electrolysis, solvent extraction, biosorption, reverse osmosis, and adsorption, etc. (Mohan and Chander 2006; Ríos et al. 2008; references therein). However, adsorption turns out to be the most preferred one for the removal of metals because of its simplicity and efficient mechanism (Mohan

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and Chander 2006; Heping et al. 2006). The adsorption process becomes more viable on commercial scales when the adsorbents are easily available and economically feasible (Bailey et al. 1999; Ríos et al. 2008; Mohan and Gandhimathi 2009). Coal fly ash is one such suitable adsorbent which is gaining increasing attention because it is the most abundant waste material produced from coal-fired thermal power plants (Cho et al. 2005; Montagnaro and Santoro 2009; Mohan and Gandhimathi 2009). Its major chemical components such as alumina, silica, iron oxide, and carbon and physical properties such as porosity, particle size, and surface area make it a potential agent for the adsorption of metals from contaminated water (Cetin and Pehlivan 2007; Ahmaruzzaman 2010). The use of coal fly ash as well as synthetic products such as zeolites manufactured from fly ash, has been widely studied for their adsorption characteristics in the removal of metals from AMD or contaminated water (Moreno et al. 2001a, b; Petrik et al. 2003; Gitari et al. 2006; Perez-Lopez et al. 2007; Ríos et al. 2008). However, the raw fly ash exhibits a low adsorption capacity than synthetic products. In addition, the raw coal ash can be used only when the fly ash is alkaline in nature. Use of coal fly ash containing high-unburned carbon can be a more suitable adsorbent for the removal of metals because of its high surface area and low cost (Wang and Zhu 2007).

Tertiary coals of north eastern coalfields of India are well known for their high sulfur content and consequent serious AMD problems (Equeenuddin et al. 2010; Sahoo et al. 2012). Jaintia Hills coalfield is one of them, which is the major coal producing zone in the state of Meghalaya, India. The AMD from this coalfield is strongly acidic (pH as low as 1.6) with SO_4^{2-} as the dominant anion and high concentrations of Fe, Al, Mn, Cd, Pb, and Ni (Sahoo et al. 2012), which contaminates the stream water (Fig. 1) used by the surrounding villagers for various purposes including rearing livestock. Thus, it is essential to develop some cost effective solution to

this detrimental effect of AMD. Based on the local geological material, huge quantity of fly ash, which is considered as waste, is being generated in Meghalaya. This ash contains high-unburned carbon particles. Therefore, choice of using this ash as an adsorbent is obvious. In the present work, we investigated the feasibility of using Meghalaya coal fly ash as an adsorbent for the removal of metals from AMD. The adsorption isotherms and adsorption kinetics were studied to model the adsorption process.

Materials and methods

Experimental materials

The coal fly ash (FA) was collected from electrostatic precipitators of the Captive thermal power plant (15 MW) situated in Meghalaya, India. The FA was oven-dried at 70 °C, sieved to a particle size of <500 µm and stored in a polythene bag. The raw fly ash has low neutralization potential (16 kg CaCO_3 eq/t) and poor metals removing ability (<10 % of metals removed except Fe and Al). To improve the above parameters, the ash was modified using a simple alkali activation technique following Koukouzas et al. (2010). In the modification process, fly ash was mixed thoroughly with 1 M sodium hydroxide (NaOH) solution and then the mixture was kept on a hot plate at 90 °C for 24 h. After agitation, the solid was recovered by filtration and washed thoroughly with deionized water to remove excess NaOH. The recovered product, termed as modified fly ash (MFA), was dried at 40 °C for 24 h and used for the subsequent geochemical characterization and adsorption study.

The pH of both FA and MFA was determined from their respective slurries prepared using 10 g ash mixed with 25 mL of deionized water. The specific surface area was measured using BET (Brunauer–Emmett–Teller) method and the loss on ignition was calculated by heating the pre-

Fig. 1 Contamination of a stream by acid mine drainage around Jaintia coalfield



Table 1 Laboratory prepared acid mine water (pH = 1.65)

Parameters	mg/L
Al	119
Fe	238
Zn	21.6
Mn	22
Pb	9.47
Ni	14.3

heated sample (Bayat 2002). The point of zero charge (pH_{zpc}) of both types of ash was determined by mixing 0.5 g of ash with 100 mL of deionized water in a series of beakers while adjusting the pH of the slurry from 2.5 to 7.5 using 0.1 M NaOH or 0.1 M HCl. The mixtures were shaken for 2 h and the charge potential was measured using zeta potential analyzer (Malvern nano ZS). The mineralogy of the ashes was determined employing Rigaku miniflex X-ray diffractometer (XRD) with $\text{CuK}\alpha$ radiation. Both major and minor element concentrations were obtained using an XRF Spectrometer (Philips PW 2404). The surface morphology of fly ash was observed under a scanning electron microscope (JEOL JSM-5800).

Simulated mine drainage (SMD) was prepared in the laboratory closely resembling the AMD from the Jaintia Hills coalfield by doping various concentrations of metals in the form of their respective sulfate-containing salts. All the reagents used were of analytical grade (MERCK). Deionized water from a MILLI-Q system was used in all the experiments. The chemical composition of SMD is given in Table 1.

Sorption studies

Batch sorption experiments were carried out by mixing different quantities (25, 50 g, 80, 120, and 150 g to understand the effect of adsorbent dosage; 120 g for deciphering the kinetics study; and 25, 50, 80, and 120 g for isotherm study) of MFA in 1000 ml of SMD solutions in separate conical flasks. The mixtures were agitated in a mechanical shaker (120 rpm) for 3 h at ambient temperature (27 ± 2 °C) for the effect of dose and isotherm studies, while for kinetics studies, the mixture was agitated for different periods of contact time (10, 30, 60, 120, 180, 240, 300, 360, and 420 min); then filtered using Whatman 0.45 μm filter paper. The final concentrations of Fe, Al, Mn, Ni, Zn, and Pb in the aqueous phase were determined using atomic absorption spectrophotometer (AAS). The error in analyzing these cations was within 10 %. All the sorption experiments were carried out in duplicate to ensure reproducibility. In each case, the percentage error between the two sets of experiment was within ± 10 %.

Table 2 Chemical composition of FA and MFA

	FA	MFA	Change (%)
Major component (wt%)			
SiO_2	46.3	38.1	−17.7
Al_2O_3	27.6	24.5	−11.2
Fe_2O_3	5.7	5.1	−10.5
MgO	0.3	0.28	−6.6
CaO	0.8	1.3	+38.5
K_2O	0.46	0.42	−6.5
Na_2O	0.67	5.85	+88.5
Minor elements (ppm)			
Cu	106	101	−4.7
Cd	87	65	−25
Cr	61	55	−9.8
Mn	80	67	−16.25
Zn	220	204	−7.2
Pb	119	107	−10

+, % of metals added in the MFA; −, % of metal removed from MFA

Table 3 Physical properties of fly ash untreated (FA) and after modification (MFA)

Properties	FA (%)	MFA (%)
pH	5.3	11.5
Specific surface area (m^2/g)	24.6	47.2
Loss of ignition (LOI)	17.4	20.3
pH_{zpc}	3.6	3.7
Particle size (<75 μm)	30	28
Particle size (>75 μm)	70	72

The adsorption capacity of metals was calculated as follows:

$$\text{Adsorption (\%)} = (C_i - C_f) \times 100 / C_i \quad (1)$$

where, C_i and C_f are the concentrations of the metal ions in the initial and final solutions, respectively.

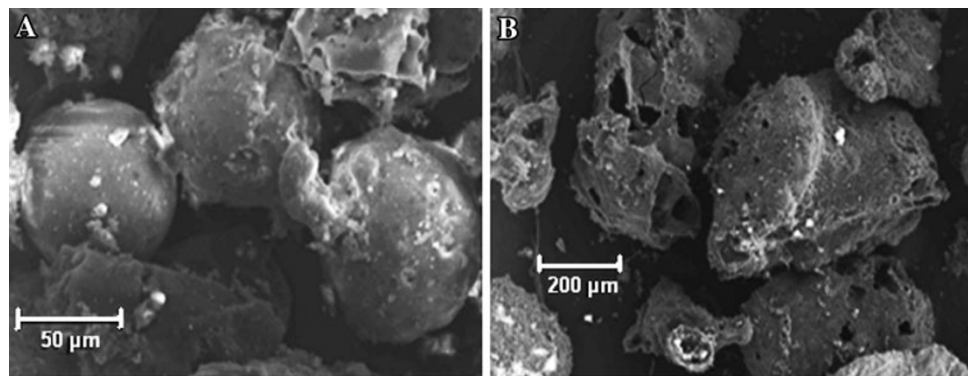
The batch adsorption experiments were also conducted with actual acid mine drainage collected from Jaintia coalfield using the optimum dosage (120 g/l) of adsorbent (MFA) in 1,000 mL of solution.

The experimental data were analyzed using adsorption isotherm such as the Freundlich and Langmuir adsorption isotherm and kinetic equations such as pseudo first-order, pseudo second-order and intra-particle diffusion equations.

Desorption experiments

The desorption experiments were carried out using the metal-loaded MFA, recovered from adsorption experiment, in both acidic and near neutral solution to estimate the metal releasing capacity of MFA. Acidic solution (pH 2)

Fig. 2 Photomicrographs of cenospheres (a) and porous structure (b) of coal ash



was prepared using 0.1 M HCl and deionized (DI) water while near neutral solution (pH 6.5) was pure DI water. In the experiment, 30 g of MFA (recovered from adsorption experiment) was treated in 1,000 mL of solution and shaken at different time intervals for 7 h. At the end of each time interval, the samples were collected, filtered and analyzed for metal concentrations using AAS. The quantity of each metal desorbed from MFA was calculated by the difference between the amount of metal ions adsorbed on the adsorbent (at the equilibrium stage during the adsorption experiments) and the metal ion concentration in desorption medium.

Results and discussion

Characterization of the materials

The chemical composition and the physical properties of FA are given in Tables 2 and 3, respectively. The FA is silicoaluminous with 46.3 % SiO₂, 27.6 % Al₂O₃, 5.7 % Fe₂O₃, and 0.8 % CaO besides containing trace amounts of Cu, Cd, Cr, Mn, Zn, and Pb. The ash is acidic in pH (pH 5.3) with high surface area (24.6 m²/g). The fly ash contained very less amount of cenospheres (Fig. 2a) formed by the condensation of aluminous and siliceous droplet in the air, but dominantly contained irregular, porous “sponge like” particles (Fig. 2b) of unburned carbon, which were concentrated in the coarser fraction. The high amounts (approximately 70 wt%) of fly ash particles in the coarser fraction (larger than 200 mesh) coupled with high loss on ignition (LOI) indicate the poor combustion efficiency at the thermal power plant. The presence of porous materials and unburned carbon results in high surface area (Wang et al. 2005; Wang and Zhu 2007). The mineralogy of ash includes quartz, anhydrite and hematite as the dominant phases (Fig. 3). In addition, presence of large and irregular background in the diffractogram of ash indicated abundance of glassy and amorphous constituents.

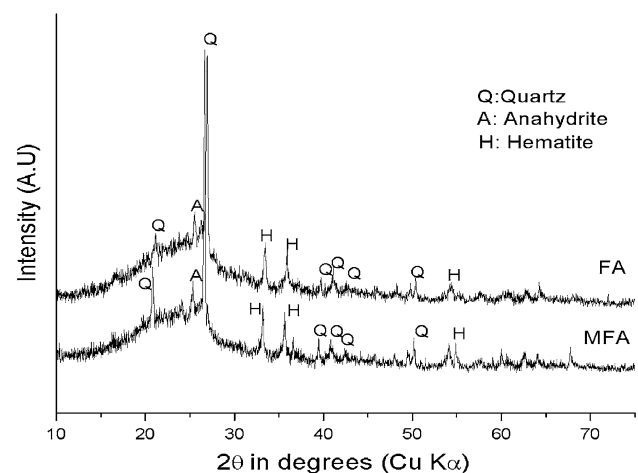


Fig. 3 Diffractograms of fly ash “untreated (FA) and “modified” (MFA)

The detailed elemental compositions of the MFA are given in Tables 2 and 3. It was observed that while alkali modification reduced the concentrations of major elements, such as Si and Al significantly, and resulted in partial leaching of elements viz. Cd, Cr, Mn, Zn, and Pb; the concentration of Na₂O increased in the MFA. The lower Si and Al concentrations in MFA indicate that MFA can be a better sorbent than raw ash for adsorption of metals, because the cation exchange capacity and pore volume are inversely related to the Si and Al concentrations (Flanigen 1991; Querol et al. 1997). Further, the pH and surface area increased near about twofold in MFA (Table 3). The particle size, particularly coarser fractions (>75 μm), is increased in “MFA” than “FA” with increasing surface area and LOI. Although, similar observation was made by Itkos et al. (2010a, b), in this study, higher surface area coupled with higher LOI in “MFA” are due to increase in a portion micropore and loss of mineral matters from ash after alkali treatment. The mineralogy (Fig. 3) and pH_{ZPC} remained unchanged irrespective of modification.

Sorption studies

The effects of various parameters such as contact time, adsorbent dose, and pH on metal adsorption process of the system are discussed below:

Effect of adsorbent dosage

The effect of adsorbent dosage (MFA) on metal adsorbed was studied by shaking a series of 1,000-mL flasks containing SAMD with different doses of MFA, varying from 25 to 150 g/L for 3 h at 27 ± 2 °C. For all these runs, initial concentration of metals in SAMD and temperature are fixed. From Fig. 4a, it was observed that the percentage of metal adsorbed gradually increases as the dose of adsorbent increases from 25 to 120 g/L and remained constant thereafter. This is probably due to increase in surface area or number of available adsorption sites with increased dosage (Ozacar and Sengil 2005). The increase in metal uptake becomes insignificant at doses above 120 g/L as observable in Fig. 4a. The increase in adsorbent dosage in a fixed volume of adsorbate reduces the number of available sites due to decrease in effective surface area (Namasivayam et al. 1998). Gupta and Bhattacharya (2006) reported similar results for Ni adsorption by ash. The minimum adsorbent dose corresponding to the

maximum removal is the optimum dose. Thus, it is found that for the quantitative removal of metals from SAMD, the optimum dose of MFA is 120 g/L.

Adsorbent recorded a maximum metal removal capacity of 89, 92, 94, 96, 60, and 99 % for Ni, Zn, Pb, Fe, Mn, and Al, respectively, at optimum dosage (120 g/L) and 180 min contact time. The pH of the adsorbate increased (pH 2.8–6.6) with adsorbent dose up to 180 min and remained constant thereafter. This may be due to the basic nature of the adsorbent.

Effect of contact time

In adsorption process, contact time is one of the important parameters that delineate the equilibrium point of metal adsorption and affect the adsorption kinetics. This was studied by shaking a series of 1,000-mL flasks containing SAMD with a fixed dose of MFA (120 g/L) at 27 ± 2 °C. Figure 4b depicts that the adsorption is heterogeneous with initial rapid rate followed by slower rates. Maximum removal of metals happened within 180 min of agitation and subsequently remained almost constant (Fig. 4b). Thus, the effective contact time or equilibrium time taken was 180 min. Within 1 h, more than 90 % of Fe, 70 % of Zn, Pb, and Ni and more than 35 % of Mn were adsorbed. The rapid adsorption rates in the initial hours are likely due to free adsorption sites are more in the initial stage, and the slow adsorption rate in later stage is due to saturation of the active adsorbent sites (Onundi et al. 2010).

Adsorption isotherms models

Adsorption isotherms describe the surface properties (heterogeneity/homogeneity) of adsorbents. In the present study, the Langmuir and Freundlich adsorption isotherms were used because these two are most widely used models due to their simplicity and ability to describe the experimental data in a wide range of concentrations (Peric et al. 2004).

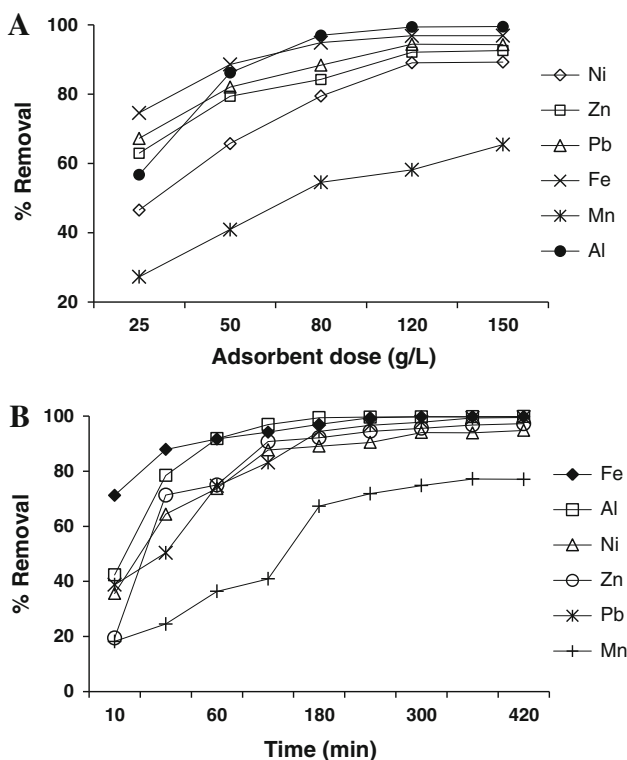


Fig. 4 Effect of the adsorbent dose on metal removal by MFA at 3-h contact time (a) and effect of contact time on metal adsorption onto MFA (b)

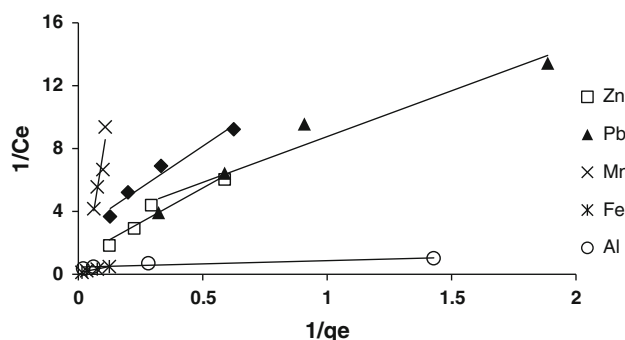


Fig. 5 Langmuir isotherm model for various metals onto MFA

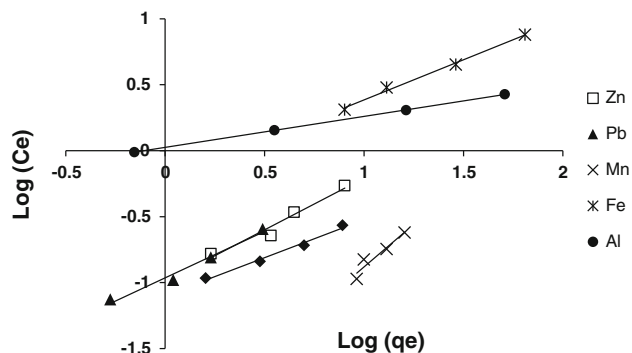


Fig. 6 Freundlich isotherm model for various metals onto MFA

Table 4 Langmuir and Freundlich isotherms parameters for Al, Mn, Ni, Pb, Fe and Zn adsorption on MFA

Metal ions	Langmuir isotherm				Freundlich isotherm		
	Q_{\max} (mg g ⁻¹)	b (l mg ⁻¹)	R^2	R_L	K_f	n	R^2
Al	2.46	0.87	0.898	0.009	0.941	4.27	0.999
Mn	0.01	-47	0.878	0.008	0.006	0.77	0.918
Ni	0.093	3.759	0.961	0.018	0.08	1.75	0.985
Pb	0.171	1.987	0.944	0.05	0.108	1.42	0.977
Fe	0.318	32.6	0.992	0.0012	0.598	1.64	0.994
Zn	0.113	8.1	0.928	0.005	0.102	1.27	0.958

The plot of the isotherms is shown in Figs. 5 and 6 and model parameters are contained in Table 4. The results showed that Langmuir isotherm was found to be linear over the concentration studied with low correlation coefficients (R^2) than that of Freundlich isotherm model (Table 4). This indicates that monolayer adsorption occurring at specific homogeneous sites on the adsorbent is not favoring (Langmuir 1916). According to the Q_{\max} , sorption onto MFA indicates the following adsorption sequence: Al > Fe > Pb > Zn > Ni > Mn.

An essential characteristic of Langmuir isotherm can be presented in a dimensionless constant called separation factor (R_L). For favorable adsorption $0 < R_L < 1$; whereas, $R_L \geq 1$ depicts unfavorable and linear adsorption and $R_L = 0$ describes unfavorable but irreversible adsorption (Kadirvelu and Namasivayam 2003). From the calculated R_L , it is inferred that adsorption of all metals onto MFA is favorable being high in the case of Al.

From Fig. 6 and Table 4, it is observed that the values of R^2 of Freundlich isotherms for all metals are high except Mn, indicating that the data fit well with the Freundlich isotherm model, giving an expression of surface heterogeneity as well as multilayer of adsorption characteristics (Freundlich 1906). Values of ' n ' between 1 and 10 represent good degree of adsorption (Erdem et al. 2004) and

comparing this with values obtained (Table 4), it can be said that the data indicate good adsorption of all metals onto MFA except Mn. Furthermore ' K_f ', a constant related to adsorption capacity, shows the sequence Al > Fe > Pb > Zn > Ni > Mn. From the above study, it was found that the adsorption of metals is controlled by the heterogeneous nature of the adsorbent with an exponential distribution of adsorption energy on the surface sites.

Effect of competing cations on adsorption

Keeping in view that the acid mine drainage is multi-component in nature with various metals in solution at varying concentrations; it is pertinent to observe the influence of competing ions on the individual metal adsorption onto MFA. The adsorption efficiency of both single and multicomponent solutions are compared and presented (Fig. 7). The lowering of adsorption of metals (in %) in multicomponent solutions are 0.78, 1.4, 66, 35.9, 27, and 25 for these metals Fe, Al, Mn, Zn, Ni and Pb, respectively, compared to their corresponding single component solutions. These values indicate Fe and Al are unaffected by competing ions relative to other metals. This is probably due to removal of Fe and Al through precipitation rather than adsorption. The adsorptions of other ions were significantly affected suggesting different kinds of adsorption mechanism to be involved in the process (Amarasinghe and Williams 2007). Subsequently, the kinetics of the adsorption process was analyzed.

Adsorption kinetics

In order to investigate the rate-limiting mechanisms in the adsorption process, the kinetic models, such as the pseudo first-order (Lagergren 1889), pseudo second-order (Ho and McKay 1999) and intra-particle diffusion (Weber and Morris 1963) were tested. These three models are currently widely used for adsorption systems due to its good

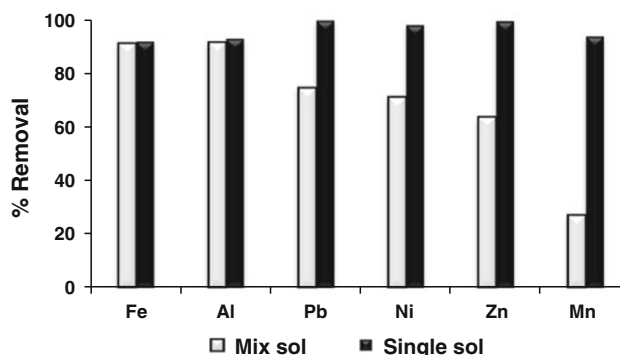


Fig. 7 Comparison of the adsorption of metals from single and multi-element solution (*sol* solution)

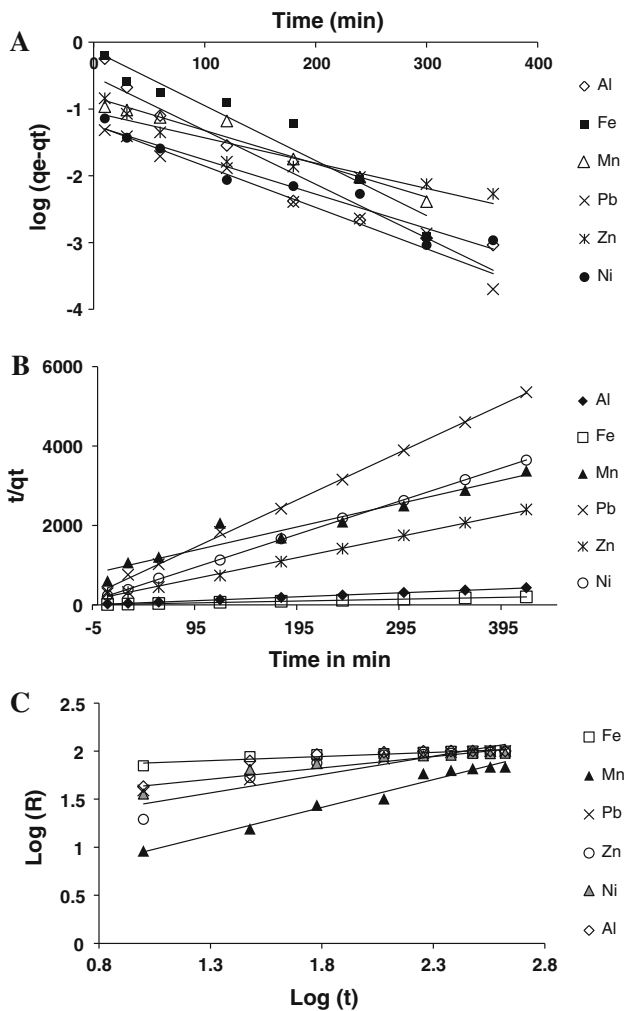


Fig. 8 Pseudo first-order plot (a), pseudo second-order plot (b) and intra-particle diffusion model (c) of various metals onto MFA

representation of the experimental data for most of the adsorbent adsorbate systems.

From the plot (Fig. 8a, b) and the equilibrium parameters calculated thereof (Table 5) for various metals, it was found that the linear correlation coefficient (R^2) of pseudo second-order model for all metals (except Mn) is relatively

high ($R^2 > 0.99$) compared to the pseudo first-order model. Also, the calculated q_e were in good agreement with experimental q_e (Table 5) of pseudo second-order reactions, except for Mn. This shows that except for Mn, the adsorption of Pb, Zn, Ni, Al and Fe followed pseudo second-order type reactions indicating chemisorption as the rate-limiting step, indicating that the adsorption capacity is proportional to the active sites on the surface of the adsorbent (Ho and McKay 1999). Kinetic constants generated (Table 5) from the slope and intercept of the plot suggest higher reaction rate and hence greater adsorption with higher k_2 while lower q_e indicates higher absorption capacity (Mohan and Gandhimathi 2009). Hence, the order of adsorption is Ni > Pb > Zn > Al > Fe > Mn.

From Fig. 8c and Table 5, it was observed that intra-particle diffusion model describes Mn better than the others, as the correlation coefficient (R^2) of Mn for intra-particle diffusion model is higher than pseudo first-order and pseudo second-order kinetic models. Larger value of 'a' indicates a better mechanism since 'a' < 0.5 indicates that the intra-particle diffusion is not the only rate-limiting step (Kobya 2004). From Table 4, it is observed that only Mn exceeded the value of 0.5, indicating the rate-limiting step may be intra-particle diffusion for it, indicating that a transport process that involves the movement of this ion from the bulk of the solution into the interior pore of the adsorbent (Kaczala et al. 2009).

Mechanism of metal adsorption

Coal fly ash adsorbs metals mainly due to its carbon content (Wang et al. 2004) besides the functional oxide groups viz. SiO_2 and Al_2O_3 (Bayat 2002). Silica surface is positively charged in low pH and negatively charged at high pH (Mohan and Gandhimathi 2009). The zero point charge (pH_{ZPC}) of silica is generally two. Similarly, Al and Fe also develop surface charges depending on the pH. This indicates that silica and alumina in the adsorbent, above their respective pH_{ZPC} , provide negative charge, which is used as suitable sites to adsorb metal and metal hydroxide on

Table 5 Adsorption kinetic model rate constants for Al, Mn, Ni, Pb, Fe and Zn

Metal ions	Pseudo first-order				pseudo second-order				intra-particle diffusion	
	q_e (exp.) (mg g ⁻¹)	k_1 (min ⁻¹)	q_e (theor.) (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	q_e (theor.) (mg g ⁻¹)	R^2	k_{id} (μg g ⁻¹ min ^{-1/2})	a	R^2
Al	0.98	0.018	0.31	0.93	0.104	1.014	0.99	34.0	0.19	0.76
Mn	0.124	0.012	0.15	0.95	0.041	0.171	0.93	2.7	0.58	0.99
Ni	0.115	0.009	0.05	0.93	0.463	0.12	0.99	25.1	0.23	0.88
Pb	0.078	0.014	0.06	0.97	0.462	0.083	0.99	22.2	0.26	0.95
Fe	2.11	0.019	0.75	0.93	0.076	2.140	0.99	61.0	0.085	0.89
Zn	0.179	0.007	0.09	0.89	0.180	0.189	0.99	11.72	0.038	0.83

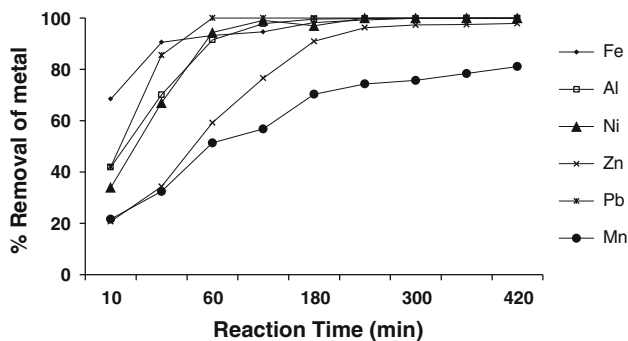
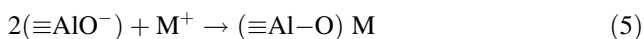
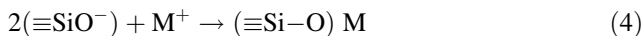
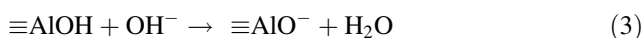
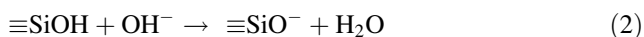
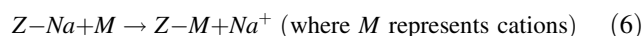


Fig. 9 Removal of metals from real AMD from Jaintia Hills coalfield by MFA

adsorbent surface (Chaiyasith et al. 2006). In this study, the pH was varied from 2.8 to 6.6. The point of zero charge (pH_{ZPC}) of MFA was 3.7. As the pH increased greater than 3.7, it can be expected that fly ash surfaces become more negative charged (Eqs. 2 and 3), which allow metals (M^+) to be complexed at the surface (Eqs. 4 and 5), leading to enhanced cationic metal ions adsorption (Chaiyasith et al. 2006; Wang et al. 2006).



Further, a possible cation-exchange mechanism can be expected in the MFA structure where more Na^+ sites available for cation exchange as shown below:



Treatment of the natural acid mine drainage

Bases on the above results of metal removal from SMD, the potential of the MFA was also evaluated using acid mine drainage from Jaintia coal field having extremely low pH (1.6) and high concentrations of Fe (243 mg/L), Al

(117 mg/L), Zn (19 mg/L), Ni (3.2 mg/L), Mn (10 mg/L), and Pb (1.9 mg/L). The experiment was conducted at the optimum dose (120 g/L). Amount of metal removed with respect to time is shown in Fig. 9. It was observed that the maximum amount of metals were removed in the first 3 h of contact and the removal efficiencies were 98, 99, 97, 90, 100, and 70 % for Fe, Al, Ni, Zn, Pb, and Mn, respectively. Hence, it indicates that MFA can be recommended as a suitable material for the treatment of acid mine drainage.

Desorption studies

Desorption studies help in assessing the recovery and reusability of the metal-loaded adsorbent, which in turn may reduce operational cost and protect the environment (Wankasi et al. 2005). In order to assess the metal desorption potential and the recyclability of MFA, desorption reagents of acid and neutral solutions were used at varying contact times. Figure 10 depicts the percentage desorption of the metal ions as a function of time from MFA. This indicates that desorption of metal ions in acidic media (Fig. 10a) was very significant than in neutral media. In acidic media, it was noticed that over 76–98 % of most of the metals, except Mn (57 %), were desorbed at the initial first 3 h, followed by slower rates thereafter. In neutral media (Fig. 10b), a very low amounts (less than 5 %) of metals, except Cd (which is less than 8.2 %), desorbed from the MFA until the end of the study time. This indicates that metal removal involves stable adsorption and complexation of the metal cations on the reactive surfaces of fly ash. The very small percentages of adsorbed metal released during the desorption tests indicated that the metal sequestered in fly ash remains stable over time. The highest recovery of metals from the MFA in acid medium is may be the fly ash becomes protonated and does not attract the positively charged metal ions, and so the protons replace the bound metal ions. Comparatively, desorption of bound metal ions from the MFA, Cd is greater than other metals in both acidic and neutral media.

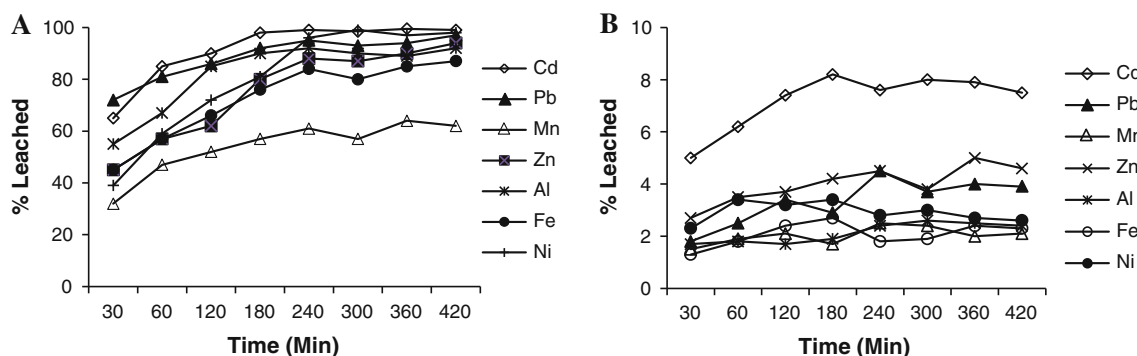


Fig. 10 Desorption of metals from MFA (used) in both acidic (a) and neutral (b) media

Conclusions

The MFA has a lower Si and Al concentrations and higher surface area and pH than the FA. Adsorption of Ni, Zn, Pb, Fe, Mn, and Al from AMD onto modified coal ash was found to be significant. The adsorption rate of metals was non-uniform with initial rapid rate for the first 3 h followed by slower rates. The removal of metal ions increases with increasing adsorbent dose; optimum dose of MFA for metal removal was found to be 120 g/L with the removal efficiency of 99, 89, 92, 94, 96, and 60 % of Al, Ni, Zn, Pb, Fe, and Mn, respectively. The results obtained from the isotherm models demonstrated that the adsorption of metals is controlled by the heterogeneous nature of the adsorbent. The adsorption rate-limiting step for Ni, Zn, Pb, Fe, and Al on MFA is chemisorption or chemical sorption, while for Mn, it is intra-particle diffusion.

Preliminary treatment of actual mine drainage revealed that the modified fly ash has the potential to be used as an effective adsorbent to treat AMD. It can also be used as a substitute of the more expensive adsorbents for the removal of metals from the contaminated water bodies as it is less costly and available locally.

The desorption experiment demonstrated that most of the metal ions were desorbed substantially in the acidic media. The applicability of MFA for metal ion removal from AMD indicates that the adsorbent can be regenerated efficiently so that the bound metal can be recovered and the adsorbent can be reused.

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