Removal and recovery of metal ions from acid mine drainage using lignite—A low cost sorbent

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Abstract

Acid mine drainage (AMD), has long been a significant environmental problem resulting from the microbial oxidation of iron pyrite in presence of water and air, affording an acidic solution that contains toxic metal ions. The main objective of this study was to remove and recover metal ions from acid mine drainage (AMD) by using lignite, a low cost sorbent. Lignite has been characterized and used for the AMD treatment. Sorption of ferrous, ferric, manganese, zinc and calcium in multi-component aqueous systems was investigated. Studies were performed at different pH to find optimum pH. To simulate industrial conditions for acid mine wastewater treatment, all the studies were performed using single and multi-columns setup in down flow mode. The empty bed contact time (EBCT) model was used for minimizing the sorbent usage. Recovery of the metal ions as well as regeneration of sorbent was achieved successfully using 0.1 M nitric acid without dismantling the columns.
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1. Introduction

Acid mine drainage (AMD) is a serious environmental problem resulting from the weathering of sulfide minerals, such as pyrite (FeS_2) and its polymorph marcasite (α-FeS). It is characterized by a low pH-value and high levels of sulfate and metals [1,2]. AMD usually contains high concentration of metals such as iron, manganese, zinc and smaller amount of cadmium, lead, copper, and nickel. The oxidation of sulfide releases dissolved ferrous iron and acidity into water which subsequently releases other metal ions. AMD's typically contain high concentration of dissolved iron which may exists either in reduced form (Fe^{2+}) or in the oxidized form (Fe^{3+}). Acidity in AMD is comprised of hydrogen ion acidity and mineral acidity (iron, aluminum, manganese, and other metal ions depending on the specific geologic setting and metal sulfide). There are 20,000–50,000 abandoned mines in the United States. Many of these mines produce acid mine drainage (AMD). These AMD contains a variety of heavy metals, which adversely affect over 23,000 km of streams in the United States [3,4]. Pennsylvania alone has over 25% of all abandoned mine sites listed by the office of Surface Mining that generates mine drainage. More than 3000 miles of rivers in Pennsylvania alone are polluted with mine drainage in the nation. If left untreated, the acid drainage can contaminate surface and ground water, damaging the health of plants, wild life, and fish [5]. When acid mine waters mix with surface waters there is potential for gross pollution. An ochre (ferric oxide) precipitate can blanket the receiving water source and kill aquatic flora and funa. The loss of biological activity could in some instances devastate the food chain and lead ultimately to fish kills and loss of amenity [6].

Iron exists in the ferric (Fe^{3+}) or ferrous (Fe^{2+}) form, depending upon the pH, and dissolved oxygen concentration. At neutral pH and in presence of oxygen, soluble Fe^{2+} is oxidized to Fe^{3+}, which readily hydrolyzes to ferric hydroxide that is insoluble in water. In most of the surface waters, Fe^{3+} predominates. Ferrous (Fe^{2+}) on the other hand is soluble and dominates under anaerobic conditions. Manganese exists in 7+, 6+, 5+, 4+, 3+, 2+, 0 oxidation states. The most common oxidation state in aqueous solu-

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Pollutant parameters	Discharge limitations 30-day average	Daily maximum
Iron	3.5	7.0
Manganese	2.0	4.0
Suspended solids	35	70
pH	$6.0 \leq pH \leq 9.0$ at all time	
Alkalinity	Alkalinity > acidity at all times	

tion is Mn(II). Even when MnO_2 (pyrolucite) is the most important form of Mn in nature, it is soluble at very low pH as Mn(II):

$$MnO_2 + 2HCl = Mn^{2+} + Cl_2 + H_2O \tag{1}$$
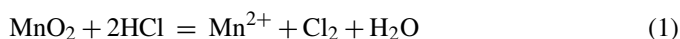
Or very alkaline conditions, to give a equimolecular amounts (dismutation) of Mn(III) and M(V). The industrial sources of manganese are steel alloy, dry cell battery, glass and ceramic, paint, ink, dye and fertilizers [7]. It also occurs in metal mines, mine drainage, especially in coal fields. The primary concerns about manganese in drinking water are its objectionable taste and its capacity to stain. The drinking water guideline recommended by American Water Works Association (AWWA) is 0.05 mg/l. The best available technology (BAT) discharge limits for acid mine wastewater (mg/l) is provided in Table 1 [8].
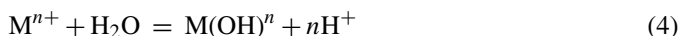
A number of methods have been used for acid mine drainage treatment including precipitation [4,9,10], electrochemical remediation [11], oxidation and hydrolysis [12–15], neutralization [16,17], ion exchange and solvent extraction [18–20], ion exchange and precipitation [21,22], titration [23], biosorption [24–27], adsorption [1,28–37], reverse osmosis [38]. Other methods used for the treatment of acid mine wastewater are also reviewed [6,39,40]. Adsorption has evolved as the preferred method for metal ions removal. Due to the high cost of activated carbon for water treatment, a search for substitutes is underway. Such adsorbents should be readily available, economically feasible, and should be regenerated with ease.

Several investigators have studied less expensive materials for the removal of Fe(II), Fe(III), Mn(II) from water such as zeolites [41,42], activated sludge [43], collophane [44], hydrous manganese dioxide [45], and zero valent iron [46]. Other efforts made in this direction are described in various review articles [47,48].

The use of lignite in wastewater treatment has received increasing attention over the last several years [49–51]. Besides being plentiful, inexpensive lignite possesses several characteristics that make it effective media for the removal of aqueous metals from wastewater. Lignites possess a high oxygen content, which is fixed in carboxyl and hydroxyl groups. These groups are infect the active centers of the ion exchange. So the lignite materials can be used as alternative cation exchangers [52–54]. Carboxyl or hydroxyl groups are able to take part in the ion exchange reaction in the following manner (Eqs. (2)–(4))

$$nL–COOH + M^{n+} = nL–COOM + nH^+ \tag{2}$$

$$nL–COOH + M^{n+} = (n-1)L–COOM(OH) \tag{3}$$
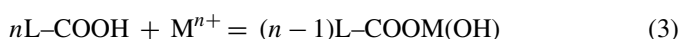
Formation of hydroxilated species may be also considered

$$M^{n+} + H_2O = M(OH)^n + nH^+ \tag{4}$$

These reactions lead to the acidification of the solution after adsorption. The dissociation constant (pK_a) of carboxylic groups are generally in between 4 and 6. Thus the increase of $[H^+]$ in solution is due to Eq. (1). Use of this material in removing the metal ions from acid mine wastewater has been investigated and the results are presented in this article. Present studies were aimed for those acid mine drainages which are contaminated by iron [Fe(II) and Fe(III)], manganese, calcium and not aluminum.

2. Materials and methods

2.1. Chemicals, materials and equipment

The lignite sample used in this study was obtained from Martin Lake, Texas. Prior to adsorption studies the samples were powdered to minus 325 B.S.S mesh. The chemicals were AR-grade. Stock solutions of the test reagents were made in deionized water from Millipipore-Q^{TM}. The pH was adjusted using dilute sulfuric acid and sodium hydroxide. The pH measurements were carried out using pH meter-model 710, Orion, USA. The metal concentrations in the samples were determined using Inductive Coupled Plasma (ICP) Spectrophotometer (Leeman PS 3000UV, USA). The carbon, hydrogen and nitrogen (CHN) analysis was carried out on LECO CHN analyzer, and XRD line profile analysis was performed using a Rigaku Geigerflex X-ray diffractometer.

3. Sorption procedure

3.1. pH optimization

The removal of Fe(II), Fe(III), Mn(II) and Ca(II) at different pH was studied in batch mode. Initial concentration of 100 ppm for Fe(II) and Mn(II) and 60 ppm for Fe(III) was used. A 25-ml of test solution of fixed concentrations was treated with 0.15 g of lignite and agitated intermittently for 48 h. The contact time and conditions were selected on the basis of preliminary experiments, which demonstrated that equilibrium was established in 48 h. After this period the solution was filtered using Whatman No. 42 and analyzed using ICP. The metal concentration retained in the sorbent phase (q_e, mg/g) was calculated by using Eq. (5)

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{5}$$

where C_0 and C_e are the initial and final (equilibrium) concentrations of the metal ion in solution (M), V the solution volume (l) and m is the mass of lignite (g).

3.2. Fixed bed studies

To determine the adsorption capacity of lignite under flow conditions, column experiments were performed in down flow mode. Both single and multi-columns were used to identify various design parameters.
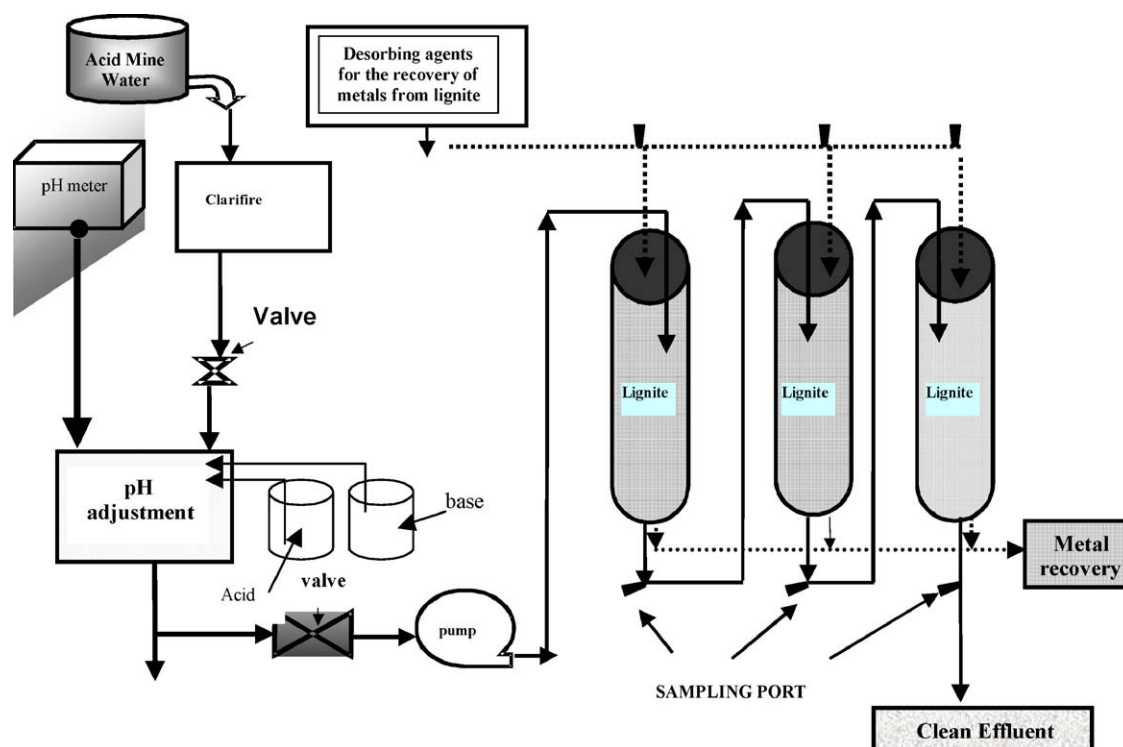
Fig. 1. Design of lignite fixed bed adsorbers (three bed system) used for the AMD treatment.

The columns were setup according to the following procedure.

3.2.1. Single column

Approximately 10 g (dry) of (20 × 40 mesh) lignite was made into slurry with hot de-ionized water and fines were removed. The slurry was then fed slowly into the column such that the formation of air voids avoided/minimized. Glass wool was used as the column support. The fixed bed column was operated in the down flow mode. The adsorptive bed length was approximately 20-cm and the bed volume was 22-ml. A hydraulic flow rate of 2.5 ml/min was maintained using a peristaltic pump. Effluent samples were collected every 15 min, measured for pH and acidified using H_2SO_4 (0.2 N) and stored for the chemical analysis. The columns were loaded with the metal ion solution containing the desired mixture of Fe(II), Mn(II), Zn(II), and Ca((II) [approximate concentration ratios = 60:50:50:50 ppm].

3.2.2. Multi-columns

The schematic representation of the setup is presented in Fig. 1. The columns were connected in series in down flow mode. Approximately 150 g (50-g in each column, dry) of lignite was weight (20 × 40 mesh) and made into slurry with hot de-ionized water and fines were removed. The procedure described above for filling single columns was repeated for all the columns used in this test. The metal solution was fed into the first column. The length of the adsorptive bed of each column was approximately 16 cm and the bed volume of the each column was 80 ml (total 240 ml). A hydraulic flow rate of 10 ml/min was maintained using a Cole–Parmer Peristaltic Pump with master flex speed controller. Effluent samples were collected every 20 or 50 min from the third column, measured for pH and acidified using H_2SO_4 (0.2 N) and stored in 40 ml test tubes for the analysis.

4. Results and discussions

Lignite is a member of the solid fuel family and is often referred to as brown coal. Macroscopically, lignite is dark brown or black in color when moist and light brown when dry. Its density lies in the range 1.0–1.35 g/cm^3. Lignites are usually amorphous and fibrous or woody in texture. Lignite possesses high surface area, typically 100–200 m^2/g [55,56].

Lignite was ashed to eliminate organic matter prior to determining the inorganic constituents. The ash was then acid digested and analyzed by plasma emission spectroscope. The chemical analysis of lignite shows the presence of SiO_2 32.1%; Al_2O_3 13.4%; TiO_2 1.30%; CaO 17.2%; MgO 1.81%; MnO 1.81%; Fe_2O_3; 18.8%; Na_2O 0.28%; K_2O 0.23%; BaO 0.14%; SrO 0.26%; C 55.56%; H 4.83%; N 1.14%; S 0.84% [2].

X-ray diffraction analysis of the sample indicated that the lignite is composed primarily of the amorphous phase with some quartz.

4.1. ZPC and leaching characteristics

Different amounts of lignite (2, 4, 8, 16, 32 mg/l) were added into de-ionized water having different initial pH (2–10) values. Blanks with no lignite were also run with the samples. All the experiments were performed in duplicate. The test tubes were agitated intermittently for 48 h at room temperature, and then left for settling of carbons. The final pH of the solution was
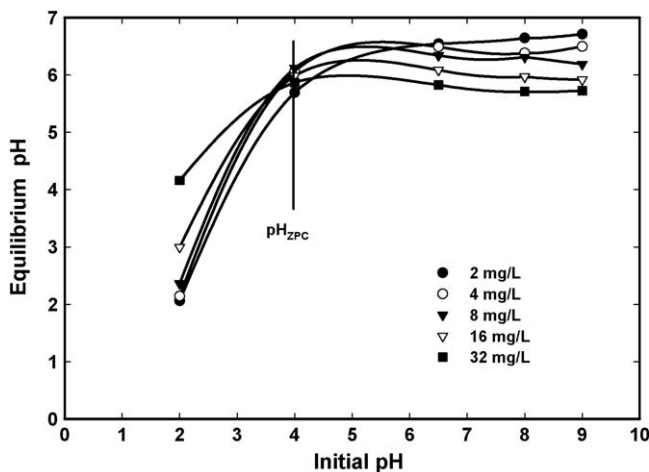
Fig. 2. Effect of amount of adsorbent on the equilibrium pH of the de-ionized waters having no metal ions [2].

measured. The variation in equilibrium pH at different lignite amounts is shown in Fig. 2. The equilibrium pH increases non-linearly in the pH range of 2–5. The increase is more pronounced in acidic medium i.e. from 2.0 to 4.0. At higher initial pH there is no increase in the solution pH [2]. The pH$_{PZC}$ was determined as the pH of the water that did not change after the contact with the samples. On the basis of this study, pH$_{ZPC}$ of lignite is considered to be pH 4.0. The equilibrium pH increases with increase in the amount of lignite at initial pH < pH$_{PZC}$, whereas it decreases with increase in the amount of lignite at pH > pH$_{PZC}$ [2].

In view of the nature of the adsorbent used, the pH change in the system must be due to the exchange interaction of lignite in the solution

$$L_2Ca + 2H^+ = L_2H_2 + Ca^{2+} \qquad (6)$$

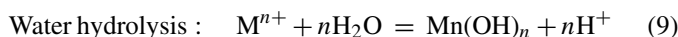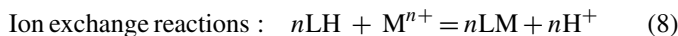$$L_2Mg + 2H^+ = L_2H_2 + Mg^{2+} \qquad (7)$$
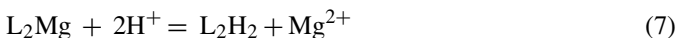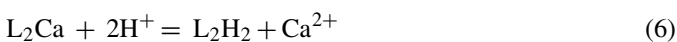
These reactions are likely to occur from left to right in strongly acidic medium due to the high concentration of hydrogen ions. As result calcium, magnesium, sodium, aluminum and potassium ions are released into the solution (Fig. 3). It is evident from Fig. 3 that the leaching of these metals is directly proportional (except for Al^{3+}, Fe^{2+}) to the lignite's amount present in the water at varying pH values [2]. The change in concentration of Al^{3+}, Fe^{2+} was more complex due to simultaneous leaching and sorption of these ions [2].

4.2. Effect of pH

The removal of Fe(II) and Mn(II) at different pH values is shown in Fig. 4(a)–(c). The sorption of Fe(II), Mn(II) and Fe(III) on lignite increases with the increase in pH. For sorption studies, the pH must be less than the pH for precipitation of respective metal ions. The sorption of Fe(II) is very low at pH$_{in}$ ≤ 2, it increases from 6% to 84% (Fig. 4(a)) at pH 4.0. At pH$_{in}$ > 4.0 the removal takes place by sorption as well as precipitation i.e. the OH$^-$ ions from the solution formed some complexes with Fe(II). Also in the acid range pH$_{fin}$ increases with the increas-

ing pH$_{in}$, i.e. neutralization and sorption process are parallel processes. The optimum initial pH chosen for Fe(II) was 3.5, to correlate the removal with sorption process. The sorption of Mn(II) at different initial pH is shown in Fig. 4(b). Similar to Fe(II) the removal is negligible at low pH$_{in}$ ≤ 2 and it increases with the increase in pH$_{in}$ and at pH$_{in}$ ≥ 8.0 precipitation occurs [2]. Therefore the optimum pH chosen for sorption studies was 6.0. Also pH$_{fin}$ increases in more acidic pH$_{in}$ and after pH$_{in}$ 4.0, the pH$_{fin}$ becomes more or less constant. Less removal of these ions at low pH have been attributed in this study to the competition between the protons and the metal ions. The removal of Fe(III) at different initial pH is shown in Fig. 4(c). The sorption is different from the other two metal ions. There is a sudden increase in the sorption process at pH 2.0, and pH$_{in}$ ≥ 3.0 precipitation as well as sorption takes place [2]. The equilibrium pH also increases in the pH$_{in}$ range 2–3. The optimum initial pH chosen for the equilibrium studies was 2.7–2.8 to correlate removal with the adsorption process. Further, decrease in pH as a function of metal concentration is likely due to two equilibria:

Ion exchange reactions : $\quad n\text{LH} + \text{M}^{n+} = n\text{LM} + n\text{H}^+ \qquad (8)$

Water hydrolysis : $\quad \text{M}^{n+} + n\text{H}_2\text{O} = \text{Mn(OH)}_n + n\text{H}^+ \qquad (9)$

Also the chemistry of Fe(II) is unimportant in aqueous solution. In water, it oxidizes rapidly to Fe(III) (E^0 Fe(III)/Fe(II) = 0.771 V). Fe(III) is a very acidic cation, and tends to precipitate as Fe(OH)$_3$ (pK_{ps} = 35) decreasing strongly the pH as shown in Fig. 4(c).

4.3. Multi-component fixed bed sorption

In acid mine drainage other metal ions are also present besides iron and manganese, therefore it is desirable to determine the effect of other metal ions on sorption by lignite. The sorption in multi-component systems is complicated because of the solute–solute competition and the solute–surface interactions. Multi-component interactions take place at the active adsorption sites where the solid–liquid phase equilibrium will emerge showing a different capacity of single metal ion. The interpretation of the multi-component systems has proved to be complex and may be the function of one or all of the following parameters: ionic radii, electronegativity, pH and the availability of active sites on the adsorbent.

Two types of column tests were performed in this study: (a) single column test and (b) multiple columns test. The column was prepared according to the procedure given in Section 2. The sorbable impurities are removed as the liquid passes through the adsorbent bed, and the portion of the bed in which sorption is occurring is defined as the mass transfer sorption zone or MTZ.

The breakthrough curves for single and three column systems are presented in Figs. 5 and 6 Figs. 5(a) and 6(a), respectively in terms of dimensionless concentration (C_e/C_0) versus effluent volume. Also the change in pH with effluent volume is presented in Figs. 5(b) and 6(b). In single column the sorption behavior was found to be quite different than that of three column systems due to the difference in empty bed contact time. In single col-
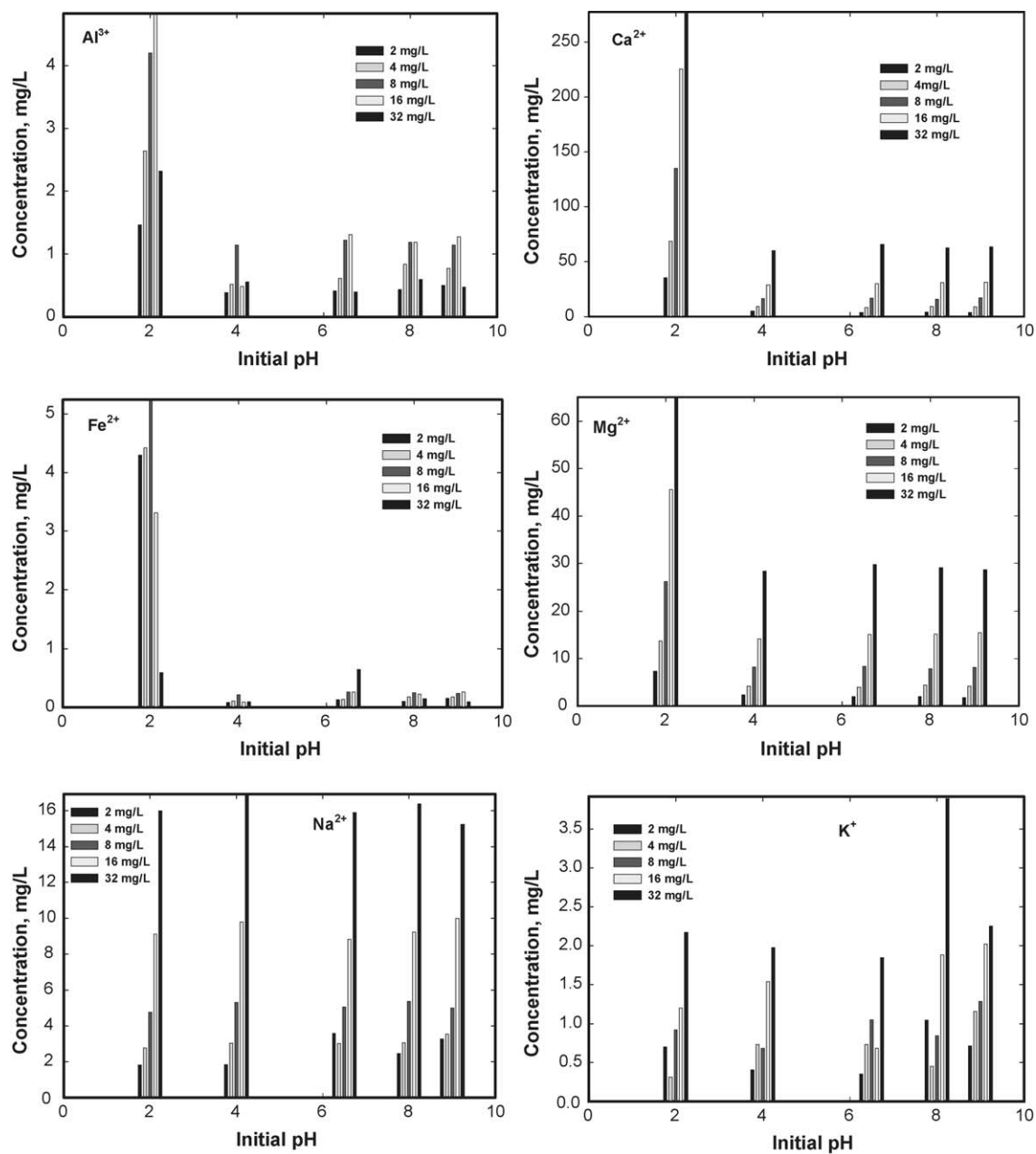
Fig. 3. Leaching behavior of lignite [2].

umn test, where the empty bed contact time is very low (9 min), the sorption of all the metal ions was found to be relatively small with the highest sorption of Fe(II) among them and the breakthrough occurred quickly. The sorption follows the order: Fe(II) > Zn(II) > Mn(II)

In the three column test, where the empty bed contact time was 24 min (Table 2) 'overshoot', a condition where the more highly retained Fe(II) displaced the previously adsorbed Mn(II) and Zn(II) take place. This phenomenon is commonly observed with adsorption of organic compounds. Thus it may be concluded that lignite initially adsorbs Mn(II) and Zn(II) can be desorbed as concentration of Fe(II) in the liquid in contact with lignite increases. The change in pH_{fin} with effluent volume is presented in Figs. 5(b) and 6(b) for single and three column sys-

tems, respectively. It was noticed that effluent pH decreased from 7.5 and 6.5 for single and three column systems at the beginning of column operation to 4.7 and 4.0, respectively. Thus it can be concluded that more is the sorption higher will be the pH_{fin} and vice versa. These results are consistent with the batch results.

The column capacity was determined by taking the total area to the point where the effluent plot joins the effluent and dividing this value by the weight of the adsorbent in the column. The performance of the columns in terms of capacity, bed volumes, breakthrough volumes, etc. is presented in Table 2. The higher capacity in case of three column systems is due to the fact that empty bed contact time is much higher in comparison to the single column system.
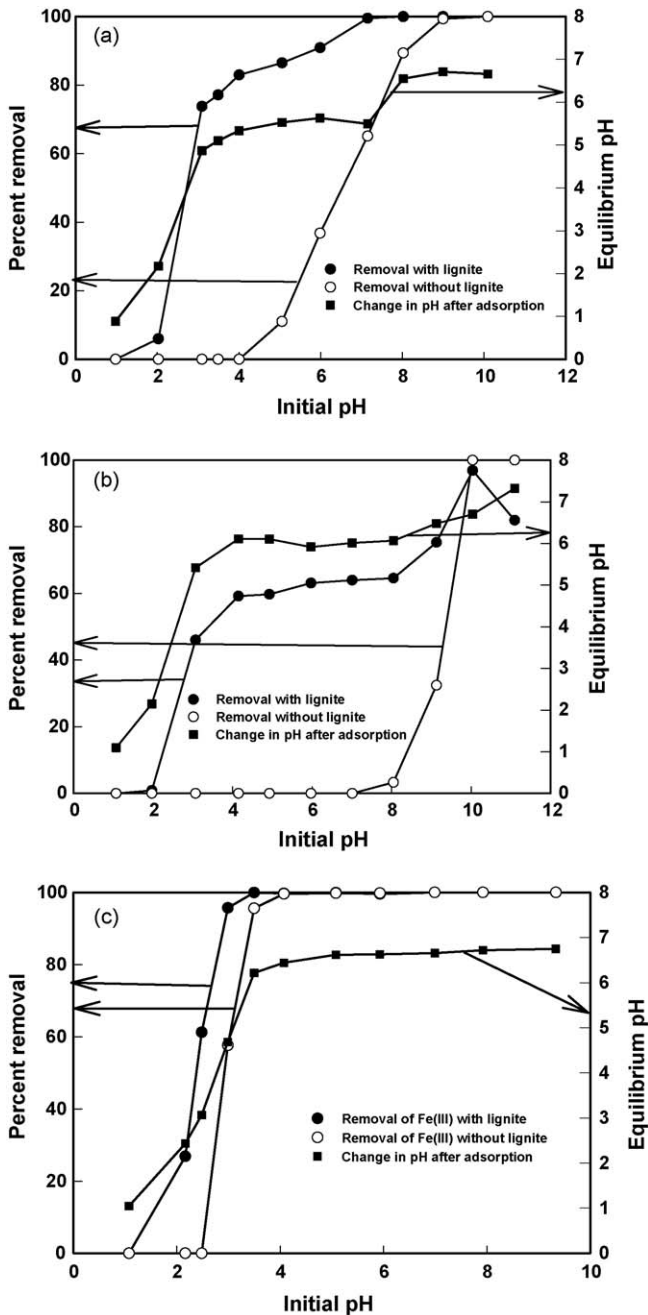
Fig. 4. Effect of pH on the adsorption of (a) Fe(II), (b) Mn(II) (100 mg/l and lignite dose 6 g/l), and (c) Fe(III) (50 mg/l and lignite dose 6 g/l) on lignite [2].
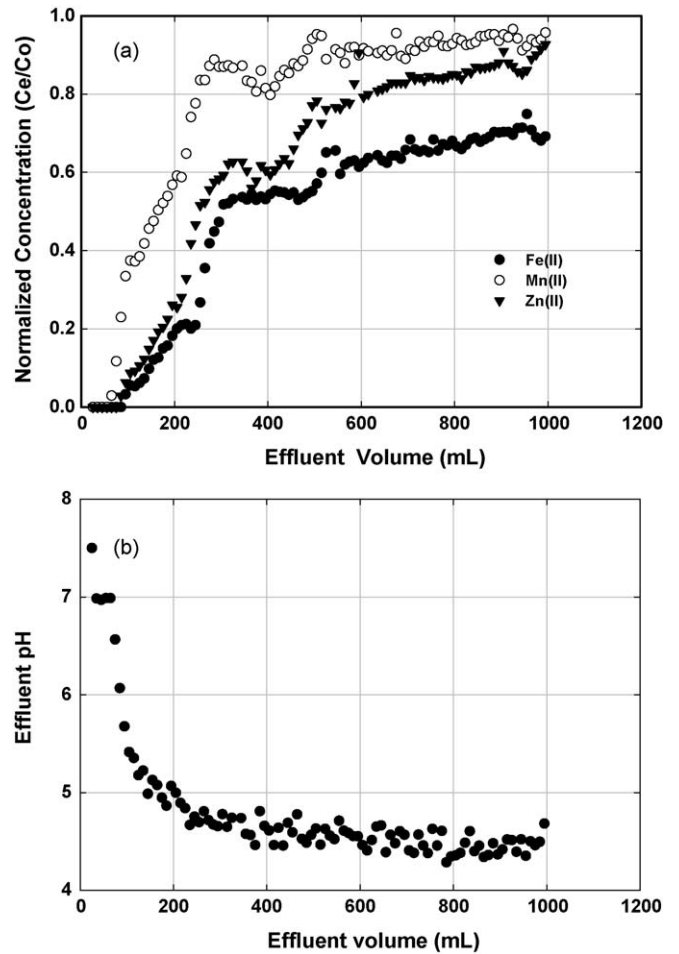

Fig. 5. Fixed bed (a) breakthrough and (b) effluent pH curves for multi-component metal ions ($Fe^{2+} + Mn^{2+} + Ca^{2+} + Zn^{2+}$) adsorption at 25 °C and pH 3.5 in single column.

4.3.1. Lignite usage rate

The lignite usage rate (LUR) defined as a parameter similar to the carbon usage rate (CUR), determines the rate at which lignite would be exhausted and how often the lignite must be changed or regenerated. The LUR may be determined from the following relation:

Lignite usage rate (lb/1000 gal)

$$= \frac{\text{Weight of lignite in column (lb)}}{\text{Volume at breakthrough (gal)}} \times 1000$$

or

$$\text{Lignite usage rate (g/l)} = \frac{\text{Weight of lignite in column (g)}}{\text{Volume at breakthrough (l)}}$$

Table 2
Column performance of lignite for multi-component adsorption of metal ions

Types of column	Bed volume (ml)	EBCT[a] (min)	Volumetric flow rate, Q (ml/min)	Effluent volume at break through point	Carbon usage rate (lb/1000 gal)	Carbon usage rate (g/l)	Total bed volumes at break through point	Column capacity (mg/g)
Single column	22	9	2.7	85 ml	979	0.981	4.0	3.4
Three column system	235	24	10	151	84	0.085	63	18.7

[a] Empty bed contact time or residence time.
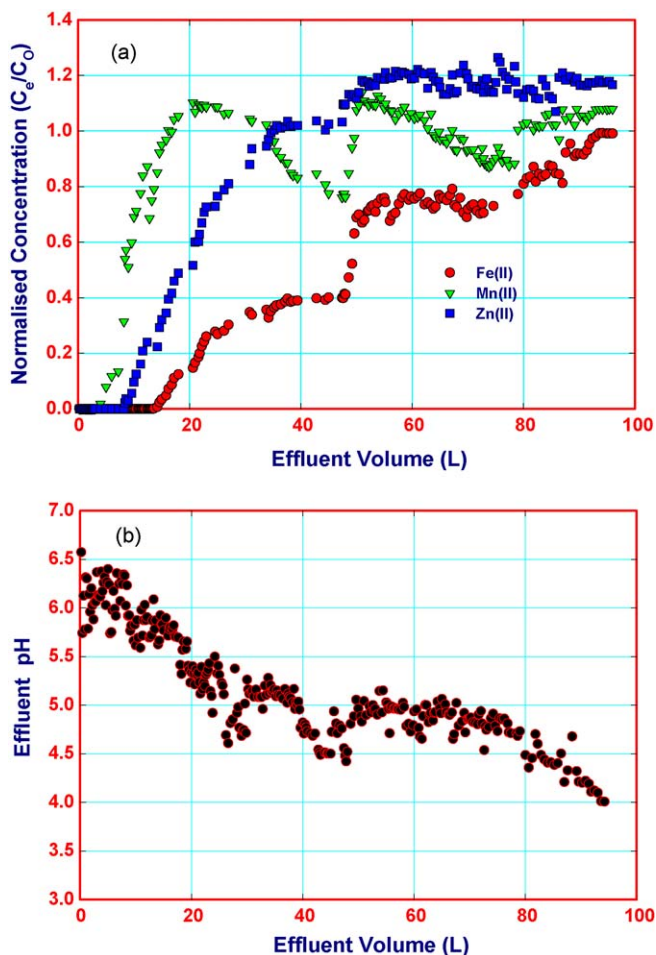
Fig. 6. Fixed bed (a) breakthrough and (b) effluent pH curves for multi-component metal ions $(Fe^{2+} + Mn^{2+} + Ca^{2+} + Zn^{2+})$ adsorption at 25 °C and pH 3.5 in three columns system.

The usage rate in lb/gal or g/l for both the systems is presented in Table 2. It is noted that in single column the usage rate is very high in comparison to three column systems. The operating line concept can be used to optimize the basic design to achieve the lowest cost. The operating line approaches a minimum on both axes in Fig. 7. The minimum exhaustion rate for a given sorption duty is that, which is achieved when the exhausted adsorbent is in equilibrium with the influent liquid, and the minimum retention time represents the minimum time for the solution to pass through the minimum volume of lignite necessary to achieve the desired level of purity at infinitely high adsorbent exhaustion rates. It can be noticed that there is an initial rapid decrease in usage rate with increase in EBCT. Thus from this data the EBCT used for the design of the contractor may be taken at the EBCT at the lowest carbon usage rate. This help in optimization of the process design which requires economic evaluation of the benefits of increasing EBCT (Fig. 7).

4.4. Sorption mechanism

Ion exchange is considered to be the most predominant mechanism in the sorption of Fe^{2+}, Mn^{2+}, Fe^{3+} and Zn^{2+} on lignite.
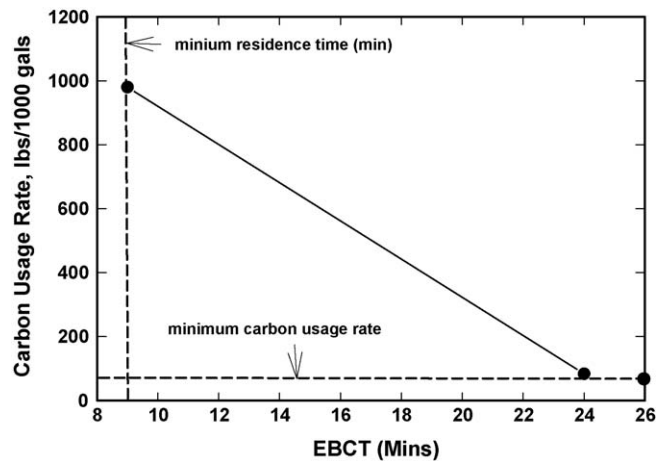

Fig. 7. EBRT operating line plot.

It was observed that during the sorption of Fe^{2+}, Mn^{2+}, Fe^{3+}, and Zn^{2+}, calcium ions were mainly released from lignite in single, binary and ternary systems [2]. Besides Ca(II) some other light metal ions such as Al^{3+}, Fe^{2+}, K^+, Mg^{2+}, and Na^+ were also released from lignite in a very insignificant amount. The sequence of this ion exchange and quantification of ions released were studied during the sorption of Fe^{2+}, Mn^{2+} on lignite. The results showed a significant release of Ca^{2+} during the uptake of Fe^{2+}. It is very well documented in literature that pure ion exchange occurs at equimolar concentration i.e. the ratio of the metal(s) bound to lignite and released should be equal to unity. In our cases the value of the metal bound $(Fe^{2+} + 1/2H^+)$ to the surface of lignite and released $(Ca^{2+} + Mg^{2+} + 1/2Na^+)$ is equal to 1 at low concentration indicating a ion exchange mechanism [2]. But at higher concentration metal bound to the surface of lignite and released is greater than one i.e. the amount of calcium released is less than the amount of metals bound indicating that besides ion exchange some other possibilities such as precipitation, physical adsorption cannot be ruled out.

The desorption tests with de-ionized water show that only an insignificant amount of adsorbed Fe(II) and Mn(II) is desorbed. This further confirms that sorption of Fe(II), Mn(II) and Fe(III) on Lignite is mostly chemical in nature. The fact that some of the Fe/Mn desorbed at all suggests that sorption by another process as mentioned above may contribute in the overall sorption capacity of the lignite.

4.5. Desorption studies

When the adsorbent becomes exhausted or when the effluent from the adsorbent bed reaches the maximum allowable discharge level, the recovery of the adsorbent material as well as regeneration of the adsorbent becomes quite necessary. Regeneration of spent adsorbent columns is quite an important process in wastewater treatment and carbon columns are, in general, subjected to thermal regeneration. In this process 10–20% of the adsorbent is usually lost by attrition during each cycle and the recovery of the adsorbate is also not possible. Elution of adsorbate with simultaneous chemical regeneration by a suitable chemical is a definite alternative to thermal regeneration
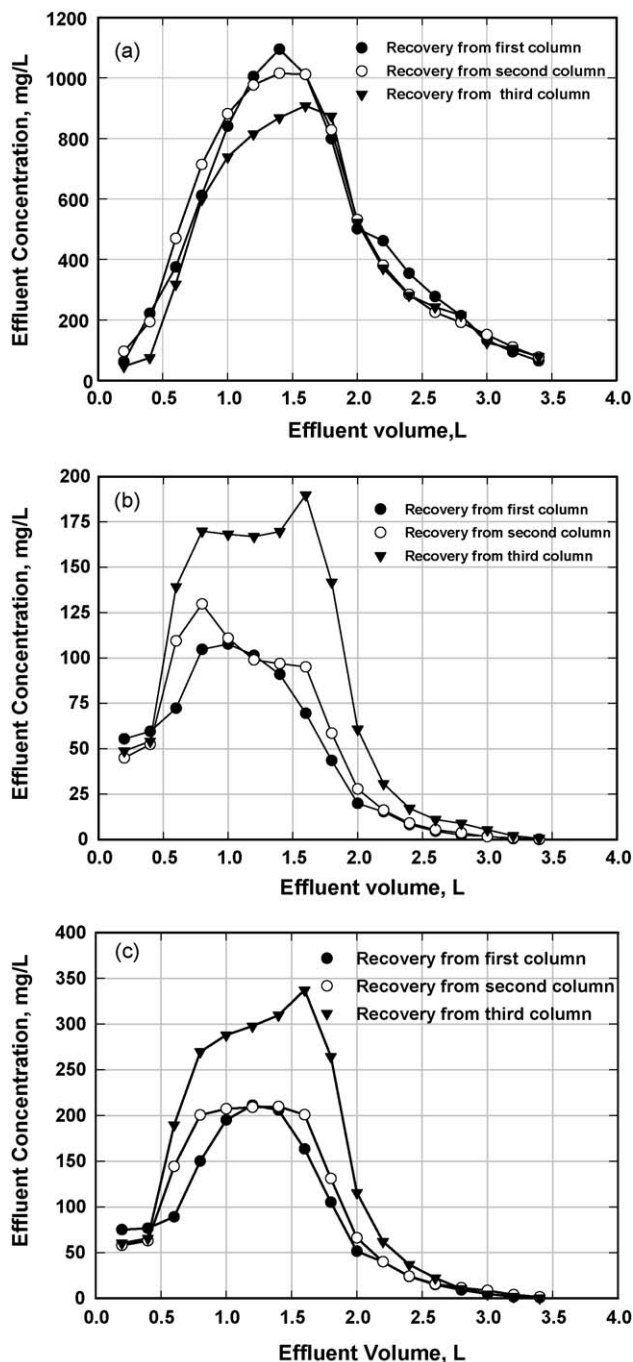
Fig. 8. Recovery of (a) Fe^{2+}, (b) Mn^{2+}, and (c) Ca^{2+} from loaded columns of lignite using 0.1 N HNO_3 at 25 °C.

and thus has been tried in these investigations. The desorption of metal ions in three column systems under identical conditions of flow rate, length of the column, etc. was tried with 0.1 N HNO_3 and the results are presented in Fig. 8(a)–(c). It is interesting to note that the recovery of the metal ions is almost 100%.

5. Conclusions

This work demonstrates that lignite can be used as a metal ion adsorbent for treating water/wastewater contaminated

with Fe(II), Fe(III) and Mn(II) in both single and multi-component systems. Studies were performed at different pH to find optimum pH. To simulate industrial conditions for acid mine wastewater treatment, all the studies were performed using single and multi-columns setup in down flow mode. The empty bed contact time (EBCT) model was applied for minimizing the sorbent usage. The desorption of metal ions in three column systems under identical conditions of flow rate, length of the column was achieved with 0.1 N HNO_3. It is interesting to note that the recovery of the metal ions was almost 100%. Desorption followed by recovery will further bring down the cost of the treatment system. The use of lignite as a value added adsorbent over its fuel value should be now considered. Large quantities of low cost adsorbents will increasingly be needed for water treatment. Lignites are inexpensive, most are non-toxic and available in large quantities. The cost of lignite is approximately $25/metric ton (http://hypertextbook.com/facts/2005/CarolineGeorges.shtml) which is much cheaper than the commercially available activated carbon costs ~$40/lb (Activated carbon 6–14 mesh 1LB; Fisher brand $40.33) (https://www1.fishersci.com). In addition, sorption capacity of lignite was superior to the commercially activated carbons tested for AMD treatment [2]. This clearly demonstrated the advantage of lignite as an adsorbent for the removal and recovery of metals from acid mine drainage.

The fundamental fixed bed adsorption parameters reported herein can now be applied for development of large-scale fixed bed reactors to obtain a reasonably high adsorption capacity even in the presence of interfering ions.

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