Removal of heavy metals from leachates using permeable reactive barriers filled with reactive organic/inorganic mixtures

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Abstract
In the present experimental study the efficiency of permeable reactive barriers (PRBs) containing organic material and limited quantities of zero valent iron, fly ash or red mud to remove heavy metals from leachates was assessed. Upflow laboratory column experiments were carried out to study the efficiency in terms of Cu, Zn, Ni and Mn removal. The columns were filled with each reactive mixture and packed slightly to simulate field conditions; synthetic solutions with initial concentration of 50 mg/L of each metal were used. Column effluents were sampled periodically and analyzed for pH, oxidation-reduction potential, sulphate and metals concentration. The experimental results show in most cases adequate metal removal efficiency. XRD analyses were used to elucidate the main removal mechanisms involved.
Keywords: heavy metals; permeable reactive barriers; organic material

1. INTRODUCTION

Reactive materials are used separately or in mixtures for remediation of contaminated wastewaters, groundwater, industrial solutions and leachates such as acid mine drainage (AMD) [1]. Reactive inorganic materials include among others zero valent iron (ZVI), limestone, red mud (RM), activated carbon, zeolite, volcanic ash and coal fly ash (FA) [2-5]. Organic materials include agricultural products and by-products, sewage sludge and organic wastes [6-9]. Combined use of organic and inorganic reactive materials may be beneficial in terms of provision of alkalinity / buffering of pH and activation of more than one removal mechanisms (e.g. precipitation and sorption) [10-12]. Organic material (CH_2O) is used as electron donor in the dissimilatory reduction of sulphates to sulphides and the alkalinity generated enables metal precipitation according to reactions (1) and (2).

$$SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow H_2S + 2H_2CO_3 \qquad (1)$$

$$Me^{2+} + H_2S \rightarrow MeS\downarrow + 2H^+ \qquad (2)$$

Zero-valent iron has been broadly used as reactive material in PRBs for groundwater remediation and demonstrates very good removal efficiency for several inorganic (e.g. Cr, Cu, Ni, As, Zn) and organic contaminants [13-15]. It consumes oxygen, according to reaction (3), establishing thus anaerobic conditions which favour growth of sulphate reducing bacteria (SRB), while the generated hydrogen according to reaction (4) can be used as electron donor in reactions involving SRB.

$$Fe^0 + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O \qquad (3)$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad (4)$$

The quantity of red mud produced during the Bayer process depends on the type of bauxite treated and varies between 0.3 t/t of bauxite for high grade and 2.5 t/t for low grade ores. Due to its texture and composition, it is characterized by high surface reactivity, but so far has scarcely been evaluated as reactive material for the removal of inorganic contaminants from AMD, contaminated plumes or industrial effluents [16-17]. Fly ash which is produced from burning of coal in fired power plants has been also used for the removal of heavy metals such as Cd, Cr, Cu, Pb, and Zn from solutions. However, its adsorption capacity is lower than that of other reactive media such as granular activated carbon and zeolite [18-19].

The efficiency of each system is affected by parameters such as pH, contaminant concentration, flow rate, temperature and retention time and can be evaluated by predicting fate of inorganic contaminants as well as by modelling the progress of the reaction front [20-21]. Optimum systems are characterized by increased reactivity, sufficient hydraulic conductivity, acceptable environmental compatibility, low cost and long-term stability [22-23]. The present paper assesses the efficiency of an organic/inorganic fixed bed for the removal of Cu, Zn, Ni and Mn from synthetic sulphate solutions.

2. MATERIALS AND METHODS

Laboratory column experiments were carried out at room temperature using goat manure (GOM), ZVI, RM and FA as reactive media. GOM used is considered as a commercial biological organic fertilizer (pH~7) containing 47% organic matter, 21×10^{12} total microorganisms/g and traces of N, P_2O_5, K_2O, Ca, Mg, Fe, Mn, Cu, B, Mo and Zn.

ZVI was purchased from Gotthart Maier, Germany. It contains Fe 92.03%, C 3.31%, Si 2.04%, Mn 0.63%, Al 0.16%, S 0.09%, Ni 0.06%, Cr 0.05%, P 0.04% and H_2O 0.4% and has a specific surface area of 482 cm^2/g. RM (-76 μm, d_{50}: 4 μm) was obtained from Aluminium of Greece S.A and has the following chemical composition: Al_2O_3 15.65%, SiO_2 6.96%, Fe_2O_3 45.58%, CaO 14.84%, MgO 0.19%, Na_2O 3.26%, K_2O 0.07%, TiO_2 7.07%, LOI 6.42%. FA (-400 μm, d_{50}: 32 μm) was obtained from Ptolemais, W. Macedonia, thermal power station and is classified as type C according to ASTM. It consists of $Fe_2O_{3(tot)}$ 5.6%, SiO_2 33.4%, Al_2O_3 13.1%, CaO 31.85%, MgO 3.67%, MnO 0.18%, Na_2O 0.46%, K_2O 0.76%, TiO_2 0.71% and SO_3 6.58% (LOI 2.7%).

Experiments were carried out in plexiglas columns (45 cm length and 5 cm internal diameter). GOM was mixed with silica sand (30% w/w) in order to optimize flow conditions within the fixed bed. No silica sand was added in case when ZVI, RM or FA were mixed (30% w/w) with GOM. The total dry weight of the reactive bed was 650 g. Two 2.5 cm thick silica sand layers were placed at the base and the top of each column in order to ensure optimum flow distribution and prevent transfer of fine particles. Up-flow was applied to ensure the required retention time, eliminate channelling and allow optimum contact between solution and reactive media.

Feed solutions were prepared by dissolving sulphate salts ($CuSO_4 \cdot 5H2O$, $NiSO_4 \cdot 6H_2O$, $MnSO_4 \cdot H_2O$, $ZnSO_4 \cdot 7H_2O$) in distilled water and pumped in the columns from 20 L plastic vessels using PROMINENT GAMMA/4 peristaltic pumps. The flow rate used was 80 mL/h so that one pore volume (~350 mL) was fed every 4.4 hours. Initial concentration of each metal in the feed was 50 mg/L. The effluents were analyzed immediately for pH, oxidation-reduction potential using HANNA pH 211 combined pH/Eh meter and electric conductivity using a HANNA EC 215 EC meter, then filtered using 0.45 μm aero disk filters, acidified with concentrated hydrochloric acid to pH<2 and stored at 4 ^{o}C until metal analysis (using a Perkin Elmer Analyst 100 flame atomic absorption spectrophotometer). Sulphate analysis was done by a LaMotte Smart2 colorimeter.

3. RESULTS AND DISCUSSION

When GOM is used as reactive medium pH of the feed increases from the initial value of 5.5 to almost 8 just after a day and then drops gradually to 6.2 (data not shown). When ZVI, RM or FA are mixed with GOM, pH after an initial increase to 8.5 drops gradually after 67 days to values around 6. RM and FA due to inherent alkalinity exhibit better than ZVI pH buffering capacity, which is reduced though under the operating pH range. Eh values (data not shown) vary in all systems between -60 mV and -20 mV and only at the end of the tests reach positive values (max. + 50 mV) indicating thus the prevalence of anaerobic conditions that favour SRB growth.

Figure 1 presents the evolution of Cu and Zn removal (%) vs. time. It is seen in Figure 1(a) that when GOM is used as reactive medium Cu removal is complete for a period of 10 days and then decreases gradually to 28% after 67 days. When GOM is mixed with FA, ZVI or RM, system efficiency improves and at the end of the test Cu removal ranges between 50% and 68%. As seen in Figure 1(b), when GOM or GOM+FA are used as reactive media Zn is completely removed for a period of 25 days; then system efficiency drops sharply and after 67 days the reactive bed becomes "exhausted". On the other hand, when GOM is mixed with ZVI no Zn is detected in the column effluent for almost 40 days. Efficiency of GOM+RM column is slightly better in the long term and Zn removal attained after 67 days is almost 60%.
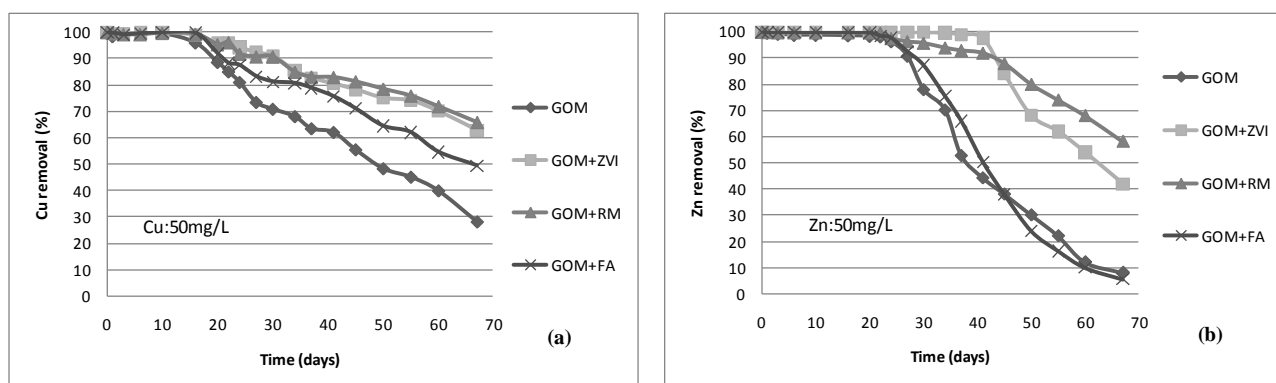

Figure 1. Evolution of Cu and Zn removal (%) vs. time

Figure 2 shows the evolution of Ni and Mn removal (%) vs. time. As seen in Figure 2(a) that when GOM is used as reactive medium Ni is completely removed the first 10 days but system efficiency drops sharply and becomes zero after 26 days. Slightly better behaviour is seen when GOM is mixed with FA, RM or ZVI. Figure 2(b) shows that all studied systems are less efficient in terms of Mn removal.
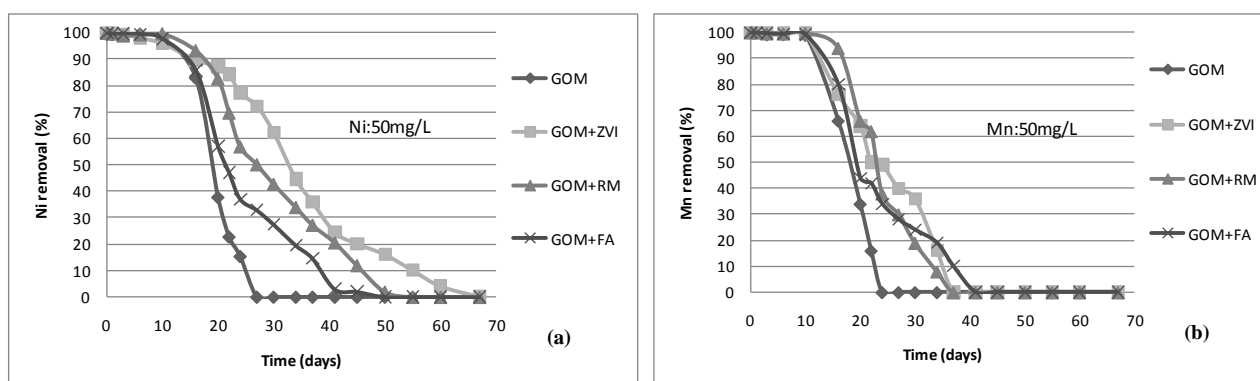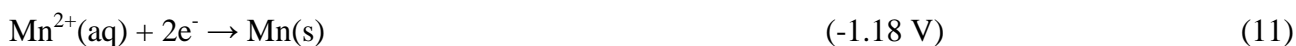

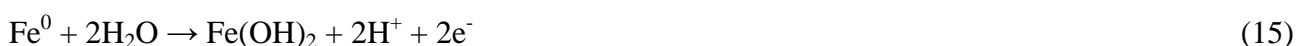**Figure 2.** Evolution of Ni and Mn removal (%) vs. time

Sorption is the main removal mechanism in all systems studied followed by precipitation of metals in the respective sulphide form. Experimental results indicate that sorption decreases in the order $Zn>Cu>Ni>Mn$. Reactions (5)-(11) show the standard reduction potential, E^o, for half reactions of the involved metal ions at 25 ^{o}C, 1 atm and 1 mol/L concentration. It is known that standard reduction potential provides a quantitative measure of a metal ion's tendency to accept electrons while ions with greater reduction potential show greater tendency for reduction.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad\qquad (0.34\ V) \qquad\qquad (5)$$

$$Cu^{2+}(aq) + e^- \rightarrow Cu^+ \qquad\qquad (0.15\ V) \qquad\qquad (6)$$

$$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s) \qquad\qquad (-0.04\ V) \qquad\qquad (9)$$

$$Ni^{2+}(aq) + e^- \rightarrow Ni(s) \qquad\qquad (-0.26\ V) \qquad\qquad (7)$$

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \qquad\qquad (-0.44\ V) \qquad\qquad (8)$$

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad\qquad (-0.76\ V) \qquad\qquad (10)$$

$$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s) \qquad\qquad (-1.18\ V) \qquad\qquad (11)$$

It is clear from the experimental data that ZVI is involved in reaction (12) that results in copper precipitation as well as in similar reactions for other metals studied. The presence though of FA and RM which exhibit complex mineralogy and higher inherent alkalinity involves dissolution of several compounds affecting thus the overall solution chemistry and triggering other secondary removal mechanisms.

$$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0 \qquad\qquad (12)$$

Due to the mild acidity of the incoming feed iron corrosion is rather limited when ZVI is mixed with GOM and thus limited precipitation of metal hydroxides or metals is anticipated. The incoming solution reacts with ZVI so that Fe^{2+} ions are transferred in solution and pH increases (reaction (13). If the incoming feed was more acidic Fe^{3+} ions would have been generated and enhanced iron corrosion would be anticipated according to reaction (14). Reaction (15) causing precipitation of $Fe(OH)_2$ and potential co-precipitation of other metal hydroxides may also take only place [15,22].

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \qquad\qquad (13)$$

$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \qquad\qquad (14)$$

$$Fe^0 + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2e^- \qquad\qquad (15)$$

The XRD pattern of exhausted GOM confirms the formation of covellite (CuS), according to reaction (2), as well as of various hydrated sulphate phases (Figure 3). Precipitation of metals as sulphides is also supported by the drop in concentration of sulphates in column effluents from the initial concentration of 160 to less than 100 mg/L (data not shown). The role of SRB is more dominant when system pH varies between 5 and 8 which is the optimum range for their growth [24-25]. The efficiency of GOM may had improved if a conditioning period of approximately 10 days was considered to allow for better adaptation of SRBs, resumption of their active metabolism and

thus increased population growth [26-27]. Sorption on the organic material is also the main metal removal mechanism in case when GOM is mixed with RM or FA. Under the pH conditions present limited dissolution of iron compounds present in RM or FA is anticipated. XRD patterns of "exhausted" GOM+RM and GOM+FA mixtures (data not shown) show the presence of covellite, tenorite (CuO) and various calcium, sodium and manganese hydrated phases.
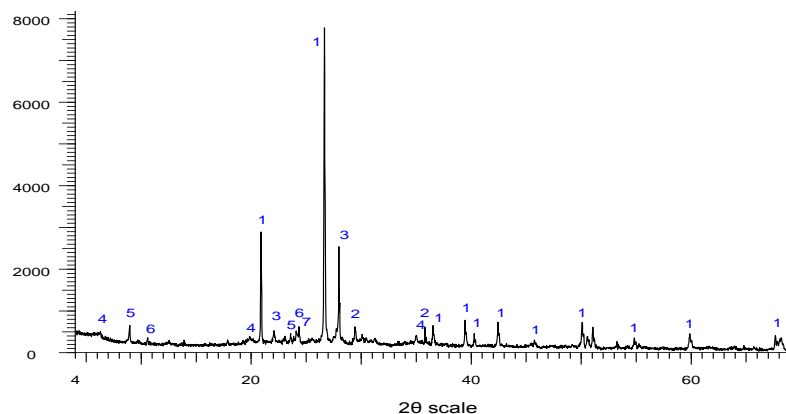
Figure 3. X-ray pattern of "exhausted" GOM (1: quartz SiO_2, 2: calcite $CaCO_3$, 3: covellite CuS, 4: chlorite $Mg_2Al_3(Si_3Al)O_{10}O_8$, 5: $Na_2(S_2O_3)(H_2O)$, 6: $K_2(S(S_2O_3)_2)(H_2O)_{1.5}$, 7: $K_2Ni(H_2O)_6(SO_4)_2$)

4. CONCLUSIONS

Permeable reactive barriers containing organic material and limited quantities of zero valent iron, fly ash or red mud show very good efficiency in decontaminating synthetic leachates containing 50 mg/L Cu, Zn, Ni and Mn. Under the experimental conditions studied sorption seems to be the dominant metal removal mechanism followed by precipitation of metal sulphides, hydroxides and other hydrated phases. Additional experiments using more acidic feed as well as geochemical studies are required to better establish the potential of each material and elucidate metal removal mechanisms.

ACKNOWLEDGEMENTS

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