

Iron Oxide-Coated Gravel Fixed Bed Column Study Performance to Remove Mixed Metals from Landfill Leachate

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Abstract. Iron oxide-coated gravel as an adsorbent was employed in continuous fixed bed column study to remove Fe(II), Ni(II), and Zn(II) simultaneously in synthetic leachate samples. Experimental and modeled adsorption capacities derived from the breakthrough curves showed the adsorption capacity order of Zn(II)>Fe(II)> Ni(II). Iron oxide-coated gravel column removed 58.24% of Zn(II), 47.71% of Fe(II), and 39.45% of Ni(II). Desorption process was studied in order to test the regeneration capability of iron oxide-coated gravel. It was seen that 99.64 % of Ni(II), 99.54% of Fe(II) and 6.75% of Zn (II) were recovered through the first cycle of adsorption/desorption. In the second cycle, the recovery rates dropped to 81.4% for Ni(II), 80% for Fe(II) and 4% for Zn(II). Based on these results, iron oxide coated gravel has potential to remove mixed metal ions simultaneously in aqueous solutions.

1 Introduction

High metal concentrations in landfill leachates stem from increasing amounts of electronic wastes, batteries, paints and treated woods in mainstream solid wastes [1, 2]. It was reported that improper management of leachate can pollute environment to a significant extent [3-5]. For that reason, reduction of these metals with effective treatment methods bears critical importance.

Removal of inorganic and organic materials from wastewater samples has been widely carried out through low cost adsorbents such as limestone, zeolite, gravel, sand, peat and industrial waste [6]. Furthermore, external coating of these materials with iron oxide causes changes in the morphology of the surfaces, and this produces novel adsorption sites having high levels of surface defects and reactive surface sites with greater intrinsic reactivity [7-9]. Iron oxide-coated adsorbents removed metals, oxyanionic metals and bacteria [9-20]. Fixed bed studies conducted with iron oxide-coated zeolite showed the removal order of Pb(II) > Cu(II) > Cd(II) > Cr(II) > Zn(II) [7]. In addition, a fixed bed column composed of iron oxy hydroxide-coated brick showed the removal order of Pb(II) > Cd(II) > Zn(II) > Fe(II) ≈ Ni(II) ≈ Cu(II) [21]. Iron oxide-coated sand in a column showed the adsorption order of Cr(VI)>As(V) [22] A column study utilizing zeolite-supported microscale zero-valent iron as adsorbent showed more adsorption for Pb(II) than Cd(II) [23]. Another study showed that almost all Cu(II) and 80% of Zn(II) could be removed in a column reactor containing iron oxide-coated gravel [19]. In a similar way, iron oxide-coated sand in a fixed bed column system removed 80% for Cu, 90% for Pb, and 98% for

Cd [24]. Moreover, iron oxide-coated sand and limestone in a column removed 98.5% of iron and 95% of arsenic [25]. Iron oxide-coated peat in up-flow columns simultaneously removed more than 99% of Cu and 90% of Zn [26]. Nano-sized iron oxide-coated sand in a continuous column study removed 90.8% of turbidity, 73.3% of Pb, 75.8% of Zn, 85.6% of Cd and 67.5% of PO₄ in a synthetic urban runoff [27]. A previously reported study showed that iron oxide-coated gravel (IOCG) in a column study showed initial removal of 96.5% of Cu(II), 94.8% of Pb(II), 90% of Cd(II), 84% of Fe(III) and 67% of Al(III) at pH 7 [28].

A limited number of studies reported the removal efficiency of IOCG in aqueous solutions for individual ions and mixed metals. Since multiple metal ions coexist together in waste water, studies aiming at simultaneous removal of mixed metals will carry more importance towards the implementation of the results in large scale systems. In this study, IOCG as an adsorbent was employed in a fixed bed column study to remove Fe(II), Ni(II), and Zn(II) simultaneously from high strength synthetic leachate samples. Adsorption/desorption studies were conducted to evaluate the reusability of IOCG. It is expected that the results of this study will provide a framework in the prediction and evaluation of simultaneous metal ions uptake with IOCG in industrial applications.

2 Materials and Methods

2.1 Filter media preparation

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The gravel used in this study was purchased from Marinara Transport, Abu Dhabi/UAE. It was made up of local rock fragments. The gravel with an average diameter of 2 mm-2.38 mm was chosen in order prevents clogs and high head losses in the filters. Surface coating of the gravel was performed following our one of previous studies [5]. The characterization of gravel and IOCG was performed using scanning electron microscope (SEM), energy-dispersive X-ray (EDX), x-Ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) surface area analysis, and the details were reported and explained in our previous studies [5, 28, 29].

2.2 Synthetic leachate preparation

The synthetic grade leachate was prepared following an established reported protocol[5]. All chemicals were purchased from Fisher Scientific and were of analytical reagent grade. An Atomic Absorption Spectrometer (AAS), Varian FS220, was used to measure the concentrations of the metal ions. The pH of the leachate samples was measured with a Hach multimeter, HQD4D.

2.3 Column adsorption studies

In this study, acrylic flow cell columns having end plate assemblies and screens made of two mesh stainless steel were used. The measurements were run in duplicates and the average values were used in the data analysis. The empty columns were cleaned with 3% of nitric acid solution to remove any residual organic contaminants. Samples of synthetic leachate were mixed with a magnetic stirrer and pumped through the columns upward using a peristaltic pump (Welch Model 3200) to be able to prevent channeling from gravity as shown in Figure 1.

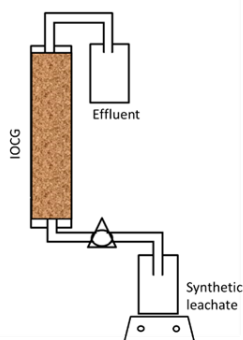


Figure 1. Column set up

The operational parameters with the column specifications are listed in Table 1. Leachate flow was stopped at time t when the concentration of a particular metal ion in the effluent reached to 98% of its initial concentration according to the formula $C_t = 0.98 \times C_0$ where C_t is the metal concentration at time t and C_0 is the initial metal concentration in the leachate sample. The pH of the samples were adjusted to 7 for the maximum efficiency of metal removal based on the result of a previous study using IOCG[5]. Effluent samples were collected at different time periods, filtered using $0.45 \mu\text{m}$

syringe filter, and then analyzed with AAS to measure the concentrations of metal ions.

Table 1. Operational parameters and column specifications for column setup

Operational Parameter	Value
Detention time (packed)	5 min
Total porosity*	0.25
Feed flow rate	15 mL/min
Operating temperature	23±1 °C
IOCG weight	107.06 gr
Active bed volume	76.96 cm ³
Total height of column	35 cm
Active height of column	15 cm
Inner diameter of the column	2.54 cm

* $p_t = (1 - V_s/V_t)$, p_t : total porosity, V_s : soil particle volume, V_t : Total volume

The total adsorbed metal ion, q_{total} (mg), is equal to the area under the plot of the adsorbed ion concentration C_{ad} ($C_{ad} = C_0 - C_t$) (mg/L) versus time (min) and can be calculated from Eq. (1):

$$q_{total} (mg) = \frac{Q \cdot A}{100} = \frac{Q}{1000} \int_0^{t_{total}} C_{ad} dt \quad (1)$$

The dynamic adsorption capacity, q_e (mg/g), was calculated from Eq (2):

$$q_e = \frac{q_{total}}{m} \quad (2)$$

The removal efficiency of ions was calculated from the ratio of total adsorbed metal ions in the column to the total amount of metal ions sent to the column based on Eq. (3):

$$Efficiency = \frac{q_{total}}{C_0 \frac{Q}{1000} t_{total}} \times 100 \quad (3)$$

The modeled column adsorption capacities were calculated based on the Thomas model given below,

$$\ln \left(\frac{C_0}{C_t} - 1 \right) = k_{Th} q_0 \frac{m}{Q} - k_{Th} C_0 t \quad (4)$$

The linear plots of $\ln [(C_0/C_t) - 1]$ versus t based on the results in column experiments were generated to derive the k_{th} and q_0 values which correspond to the slope and intercepts in the graphs.

2.4 Column desorption studies

The ability to regenerate IOCG was tested through two cycles of adsorption/desorption process. Exhausted IOCG containing adsorbed metal ions were passed through 0.1 M of HCl solution with a 15 mL/min flow rate. Effluent samples at different time periods were collected in order to determine the desorption ratio[5]. Desorption ratio was calculated based on the following formula:

$$\text{Desorption ratio(\%)}: \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100 \quad (5)$$

3 Materials and Methods

3.1 Fixed-bed column experiments

Adsorption of heavy metals by IOCG in a fixed bed column study was presented as C_t/C_0 per day as shown in Figure 2. For a constant flow rate, 96.5% removal for Zn (II) and 77% removal for Fe(II) in 5 days and 78% removal for Ni(II) in 3 days were observed during the study. Removal rates dropped afterwards. Percent removal became 0 after 21 days of operation for Fe(II), 15 days for Ni(II) and 17 days for Zn(II).

Dynamic adsorption capacity along with exhaustion times and total percent removal for metal ion on IOCG were given in Table 2. A previous study with batch experiments showed that 98.8% of Fe(II), 88% of Ni(II), and 94% of Zn(II) can be removed[5]. Furthermore, when compared with a previous batch study, it was found that the removal efficiency of IOCG in fixed-bed columns decreased as a result of decrease in contact time and decrease in contact between adsorbate and adsorbent. This situation resulted in lower retention times for the adsorption process to reach equilibrium which was also argued in another study[30].

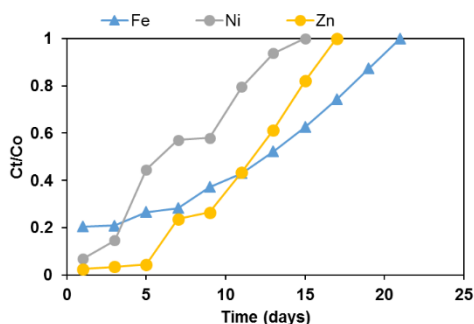


Figure 2. Breakthrough curves corresponding to Fe(II), Ni(II), and Zn(II) ions in leachate samples

Table 2. Exhaustion times, percent removals and dynamic adsorption capacity

Ions	q_e (mg/g)	t_e (days)	%Removal
Ni(II)	2.5	15	39.45
Fe(II)	11.29	21	47.71
Zn(II)	13.24	17	58.24

The dynamic adsorption capacity order for metals was Zn(II)>Fe(II)>Ni(II) which correlated with the solubility of hydroxides (pK_{sp} : Ni:15.2, Zn: 16.5, Fe²⁺:16.31) as well as the hydrated radius (Zn: 4.30Å, Ni:4.04Å, Fe²⁺:4.28Å) [31, 32]. It is apparent that the solubility products (K_{sp}) and the hydrated radius of metals are inherently related to their adsorption capabilities. Ions having smaller hydrated ionic radius are expected to diffuse easier and faster onto the surface of the adsorbent, and as a result they can accumulate in the cracks and channels more as compared to metal ions with larger hydrated radius. Ions with smaller hydrated

ionic radius are able to move closer to the adsorbent surface and easily enter the channels in the adsorbent for preferential adsorption[31]. It could be argued that Zn(II) has a strong affinity towards IOCG on the basis of its higher percent removal rate and its dynamic adsorption capacity. Lower removal efficiency of Ni(II) could be explained with the concept of charge repulsion. In aqueous solutions with pH<8, nickel ions prefers Ni²⁺ form, and they compete with H⁺ ions for the negatively charged surfaces on the IOCG. As a result, reduced Ni(II) removal rate could be observed[33]. In parallel, another study reported that Ni(II) adsorption was considerably lower in the presence of Cu(II) which competed with Ni(II) for available adsorption sites. Another reason for the lower Ni (II) removal rate could be lower retention time for Ni(II) to interact with IOCG.

It was noted that the shape of the breakthrough curve is not classical S shape. Another study reported that mixed metal solutions give different breakthrough curves[5]. Furthermore, different breakthrough curves could be obtained for a particular metal ion when other metal ions are present due to the differences in their adsorption abilities [2, 34].

The breakthrough behavior of metal ions in the leachate samples were analyzed and described in a satisfactory manner using the Thomas model. Using this model, q_0 and k_{th} corresponding to the three metal ions were calculated. It was shown that IOCG displayed high loading capacity toward these ions in the column studies in which the uptake rate ranged between 15.34 mg/g to 2.95 mg/g as shown in Table 3. A previous study showed that IOCG achieved metal ion uptakes of 66.82 mg/g for Cu(II), 26.5 mg/g for Pb(II), 23.33 mg/g for Cd(II), 1.87 mg/g for Al(III), and 0.56 mg/g for Fe(III)[28]. Other studies showed similar results; iron oxide-coated Australian zeolite performed metal ion uptakes of 0.89 mg/g for Cu(II), 0.93 mg/g for Cd(II), and 0.83 mg/g Zn (II); iron-impregnated activated carbon displayed 2.746 mg/g for Cu(II) uptake[7, 8, 14]. The correlation coefficients of Thomas model (R^2 ranging between 0.95 to 0.97) for these ions were very high, and it indicated that this model was a suitable tool to study IOCG adsorption capacities.

Table 3. Constants corresponding to the removal of metal ions in leachate using Thomas model

Ions	q_0 (mg/g)	k_{th} (L/mg.h)	R^2
Ni(II)	2.95	0.009805	0.95
Fe(II)	11.104	0.0012	0.97
Zn(II)	15.34	0.0023	0.96

A high correlation was observed between experimental and modeled adsorption capacities indicating the applicability of the Thomas model to predict IOCG sorption on metals shown in Table 4.

Table 4. Comparison of experimental and modeled adsorption capacities

Ions	q_0 (mg/g)	q_e (mg/g)
Ni(II)	2.95	2.5

Fe(II)	11.104	11.29
Zn(II)	15.34	13.24

3.2. Desorption experiments

The efficiency of metal ion recovery was tested through two cycles of adsorption/desorption process, and in the first cycle the recovery rates of 99.64 % for Ni(II), 99.54% for Fe(II) and 6.75% for Zn (II) were obtained as shown in Figure 6. In the second cycle, the recovery rates dropped to 81.4% for Ni(II), 80% for Fe(II) and 4% for Zn(II). The apparent decline in the recovery of metal ions in the second cycle could be attributed to the dissolution of iron oxide coating upon exposure to 0.1 M HCl solution for the regeneration process [7, 35]. Nevertheless, the adsorption capacity of regenerated IOCG is still high, and this finding verifies its potential for multiple cycles of metal uptake.

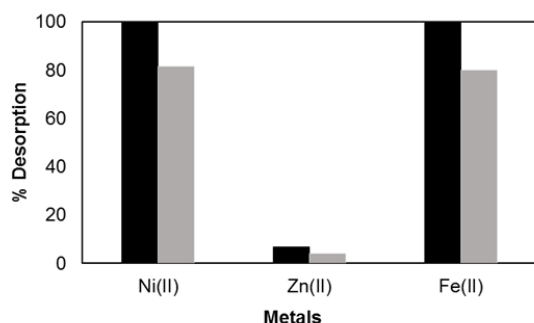


Figure 6. Desorption of metals (black color refers to first cycle and grey color refers to second cycle of adsorption/desorption process)

Nomenclature

q_e = dynamic adsorption capacity, mg/g
 C_0 = initial concentration of heavy metal (mg/L)
 V = volume of the solution (L)
 m = mass of adsorbent (g).
 q_e = max. amount adsorbed, mg/g IOCG

k_{Th} = Thomas rate constant (L/mg.h),
 q_0 = Thomas modeled column adsorption capacity (mg/g),
 C_t = outlet concentration at time t (mg/L),
 Q = flowrate (mL/min) and
 t = filtration time (min)

4. Conclusion

In this study IOCG was incorporated into column experiments in order to test its efficiency to remove multiple metal ions simultaneously in high strength leachate samples. Zn(II) ion showed the strongest affinity toward IOCG based on its high breakthrough time. Charge repulsion could be invoked to elaborate the lower removal rate of Ni(II). Loading capacities of metal ions under dynamic conditions were derived using breakthrough data, and the results showed that IOCG could effectively remove these ions. The experimental and modeled adsorption capacity order was Zn(II) > Fe(II) > Ni(II) with the average removal rate of 58.24%

for Zn(II), 47.71% for Fe(II), and 39.45% for Ni(II). The two cycles of adsorption/desorption study demonstrated that IOCG could be regenerated and reused in metal uptake studies albeit with an apparent decline in the adsorption capacity in the second cycle due to the dissolution of its iron oxide coating. Notwithstanding this observation, it seems obvious that IOCG is a potential material in the removal of metal ions simultaneously from landfill leachate. It could be incorporated into various column designs in fixed bed reactors, and it could be adapted to pilot or large-scale systems in industrial applications. In summary, our work could provide and inspire an initial framework for further studies.

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