



Removal of heavy metal ions from aqueous solutions using various low-cost adsorbents

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Abstract

The removal of single heavy metals Co and Zn from aqueous solutions using various low-cost adsorbents (Fe₂O₃, Fe₃O₄, FeS, steel wool, Mg pellets, Cu pellets, Zn pellets, Al pellets, Fe pellets, coal, and GAC) was investigated. Experiments were performed at different solution pH values (1.5–9) and metal concentrations (0.67–333 mg/l). The effect of solution pH on metal adsorption using Fe₂O₃ and Fe₃O₄ was significant, but was negligibly small using steel wool, Mg pellets, Fe pellets, and Al pellets over the entire pH range. Steel wool and Mg pellets were the most excellent adsorbents; for example, the removal of Zn and Co from dilute solutions (<35 mg/l) was greater than 94% at an adsorbent dose of 1.7 g/l. A mass transfer model, which involves two parameters τ (50% breakthrough time) and k (proportionality constant), was proposed to describe breakthrough data of Co in the fixed beds packed with steel wool and Mg pellets. The calculated breakthrough curves agreed well with the measured data (standard deviation < 6%). The value of τ decreased with increasing the flow rate. The effects of flow rates on the value of k and adsorption capacity are discussed.

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1. Introduction

Waste streams containing heavy metals are often encountered in chemical process industries such as metal finishing and plating facilities as well as mining operations and tanneries. In general, heavy metals are not biodegradable and tend to accumulate in living

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Nomenclature

F	liquid flow rate (l/min)
k	proportionality constant defined in Eq. (1) (1/min)
K_i	overall formation constant defined in Eq. (7)
$[M]$	metal concentration in the aqueous phase (mg/l)
$[M]_0$	initial or inlet metal concentration in the aqueous phase (mg/l)
Q_M	adsorption capacity of metals (mg/g)
R^2	correlation coefficient
t	breakthrough time (min)
X	fraction of metal ions remaining in the solution while passing through the bed
Y	fraction of metal ions adsorbed while passing through the bed
τ	50% breakthrough time (min)

organisms, causing various diseases and disorders. The treatment methods for metal-bearing effluents commonly include chemical precipitation (hydroxides, sulfides, etc.), membrane filtration (reverse osmosis, nanofiltration, etc.), electrolytic reduction, solvent extraction, ion exchange, and adsorption [1]. The removal of heavy metals by reverse osmosis (RO) is possible, but limitations such as the fouling of membranes and the need for pretreatment should be considered. Also, RO requires a high operating pressure. Solvent extraction and electrolytic processes are also available but they are considered to be economical only for more concentrated solutions [2]. The cost-effective alternative techniques or materials for removal of heavy metals from diluted solutions are hence needed [3,4].

Liquid-phase adsorption is one of the most efficient methods for the removal of colors, odors, organic, and inorganic pollutants from industrial effluents. Granular or powdered activated carbon is the most widely used adsorbent because of its ability to remove relatively low-molar-mass organic compounds. In general, activated carbons are not efficient in removing metallic substances unless they are chemically activated using mineral acids or transition metal salts [4]. In this case, their use is usually limited due to their high cost. This problem has led many workers to search for cheaper adsorption substitutes including fly ash, lignin, peat, natural materials (chitosan, alginate, biomass, etc.), and clays (clinoptilolite, montmorillonite, kaolinite, etc.) [3,4].

The purpose of this study was to evaluate the possibility of using some low-cost iron oxides or metal pellets such as Fe_2O_3 , Fe_3O_4 , steel wool, Mg pellets, Cu pellets, Zn pellets, Al pellets, and Fe pellets for adsorption removal of single metal ions from dilute solutions. Granular activated carbon (GAC) and coal were also adopted for comparison because of their wide use for the adsorption of organic compounds. Namasivayam and Ranganathan [5–8] have suggested the application of waste Fe(III)/Cr(III) hydroxide for adsorption removal of heavy metals such as Cr^{6+} , Ni^{2+} , Pb^{2+} , and Cd^{2+} from industrial wastewaters. In this work, batch experiments were conducted as a function of the solution pH (1.5–9) and initial single metal concentrations (0.67–333 mg/l). Dynamic experiments were performed

to obtain breakthrough curves of single heavy metals through a fixed bed packed with Mg pellets and steel wool. A two-parameter mass transfer model was proposed to describe the breakthrough data and to compare these results with the measured results.

2. Model description

An isothermal fixed bed packed randomly with the adsorbent particles was considered. In the adsorption column, the entering aqueous solution flows through the stationary adsorbent bed and some of the metal ions in the aqueous solution are adsorbed while the others pass through the bed. It is denoted that fraction of metal ions being adsorbed as Y , and the fraction of that remaining in the aqueous phase and passing through the bed as X . It is thus reasonable to assume that the rate of decrease in the adsorption of metal ions is given by [9,10]

$$-\frac{dY}{dt} = kXY \quad (1)$$

where k is proportionality constant. In Eq. (1), $X = 1 - Y$. This equation is similar to the logistic function that was originally formulated to describe the behavior of biological growth and decay [11]. This model assumes the symmetrical nature of breakthrough curves, and neglects the effect of axial dispersion. Although nonlinear, Eq. (1) can be integrated with a specific condition of $Y = Y_a$ at $t = t_a$.

$$\ln \left[\frac{Y(1 - Y_a)}{Y_a(1 - Y)} \right] = k(t_a - t) \quad (2)$$

which is the same as

$$\ln \left[\frac{X_a(1 - X)}{X(1 - X_a)} \right] = k(t_a - t) \quad (3)$$

For metal ion breakthrough at $X_a = 0.5$, the adsorption time t_a is denoted as τ , and Eq. (3) becomes

$$X = \frac{1}{1 + \exp[k(\tau - t)]} \quad (4)$$

or

$$t = \tau + \frac{1}{k} \ln \left(\frac{X}{1 - X} \right) \quad (5)$$

For the fraction of metal ions that passes through the adsorption bed, X , equals $[M]/[M]_0$ with $[M]$ being the metal concentration in aqueous solution exiting the bed at time t and $[M]_0$ being the inlet concentration. According to Eq. (5), a plot of adsorption time t versus $\ln([M]_0/[M]) - 1$ yields a straight line with the intercept and slope being τ and $1/k$, respectively.

3. Materials and methods

3.1. Adsorbents and solutions

Extra fine steel wool was purchased from Rhodes Co., USA. The particle sizes of chemical grade Fe pellets, Al pellets, Mg pellets, Zn pellets, Cu pellets, Fe₂O₃, Fe₃O₄, and FeS were all 0.18–0.83 mm (20–80 mesh). GAC (Norit model PK1-3, USA) used in this work had a particle size of 0.42–2.0 mm and a density of 0.51 g/ml. The BET surface area and the total pore volume were determined to be 1600 m²/g and 0.9 ml/g, respectively, using a sorptiometer (Micromeritics, ASAP 2010). Coal (Union Chemical Co., Taiwan) had a particle size and surface area of 0.5–2 mm and 540 m²/g, respectively. Prior to use, all adsorbents were washed with 1 M HCl, 1 M NaCl, and *n*-hexane in order to remove impurities. Then they were washed with deionized water (Millipore Milli-Q) three times. The points of zero charge of GAC and coal were approximately 6.2 and 4.3, respectively, from zeta potential measurements (Malvern, Zetasizer 3000).

Analytical grade CoCl₂, ZnCl₂, and other inorganic chemicals (HCl, NaOH, NaCl, etc.) were supplied by Merck Co. The aqueous solution was prepared by dissolving single metal chloride in deionized water. The initial pH of the solution was adjusted by adding a small amount of 0.1 M HCl or NaOH if necessary.

3.2. Batch adsorption experiments

For measuring the equilibrium amount of metals adsorbed, 0.05 g of the air-dried adsorbent was used in a batch vessel into which the solution (30 ml) was poured. This mixture was allowed to agitate at 300 rpm for 24 h in a thermo-stated shaker (Firstek, Taiwan, model B603) at 25° C. Preliminary tests showed that the adsorption reaction studied was complete after 3 min. After filtration through fiber paper, the concentrations of metals in the aqueous samples were determined using an inductively coupled plasma-atomic emission spectrophotometer (Jovin Yvon, France, model JY-38S) equipped with a flame ionization detector. The solution pH was measured using a pH meter (Horiba, Japan, model F-23). Each experiment was performed twice at least under identical conditions. The reproducibility of the measurements was generally within 3%.

3.3. Fixed bed experiments

The fixed bed tests were carried out in a water-jacketed glass column with an inside diameter of 30 mm and a length of 61 mm. The diameter of the column was approximately 50 times greater than of the adsorbent particles, so the wall effect could be ignored [12]. A typical procedure was as follows. To one end of the column, an appropriate quantity of the adsorbent (2 g) was inserted over a small glass fiber. The aqueous solution with a known metal concentration (6.7 mg/l) was fed to the top of the column at the desired flow rate (10–40 ml/min) that was driven by a micro-metering pump (Cole-Parmer, Masterflex 7518-10). Two types of fixed bed tests were carried out. The beds packed with Mg pellet and steel wool were first used to study the effect of liquid-phase flow rate. Twenty-minute fixed bed operation was selected. The rest of the tests were performed until the breakthrough

curve was completed. Samples in the outlet liquid were taken at preset time intervals and their metal ion concentrations were analyzed as described in Section 3.2.

4. Results and discussion

4.1. Metal adsorption in batch modes

Figs. 1 and 2 show the effect of equilibrium pH (pH_e) on the amount of Co and Zn adsorbed on various adsorbents. The adsorption removal of both metal ions strongly depends on solution pH using Fe_2O_3 and Fe_3O_4 over the entire pH range studied (1.5–9.0). The removal was affected more weakly by solution pH when FeS, GAC, coal, Cu pellets, and Zn pellets were used (Figs. 1 and 2). However, the removal of Co and Zn is pH-independent using steel wool, Mg pellets, Fe pellets, and Al pellets.

More than 90% of Co and Zn are adsorbed using steel wool and Mg pellets. On the other hand, the removal of Co using FeS, GAC, coal, Cu pellets, Zn pellets, and Al pellets increase slightly with increasing solution pH. Removal is within between 20 and 60%. In addition, GAC and coal are not efficient for the removal of metals (Fig. 1) although they are widely used in the treatment of organic matter. The smaller amount of metals adsorbed at low pH is probably due to competitive adsorption of H^+ with metal ions. In the case of Fe_2O_3 and Fe_3O_4 , the amounts of metals adsorbed increase sharply when the solution pH exceeds a threshold value (about 3.5 with Fe_2O_3 and 6.2 with Fe_3O_4). These results cannot be satisfactorily explained by the nature of the electrical charges on adsorbent surfaces because the zero points of charge for iron oxides are generally between 7 and 8

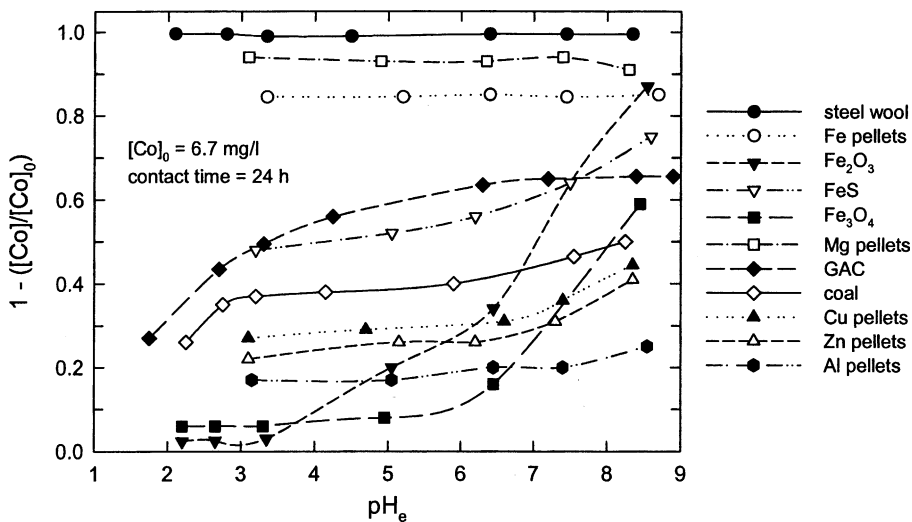


Fig. 1. Effect of solution pH on equilibrium amount of Co adsorbed using various adsorbents ($[M]_0 = 6.7 \text{ mg/l}$, adsorbent dose = 1.7 g/l).

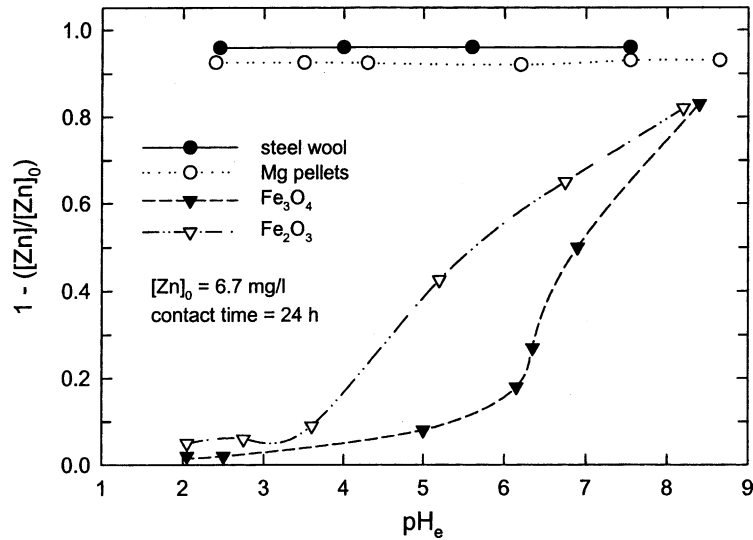
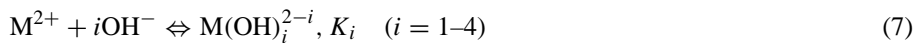


Fig. 2. Effect of solution pH on equilibrium amount of Zn adsorbed using various adsorbents ($[M]_0 = 6.7 \text{ mg/l}$, adsorbent dose = 1.7 g/l).

[13]. When the pH is greater than 6, some iron oxides may precipitate and produce $\text{Fe}(\text{OH})_2$ as colloidal suspensions with high specific surface area. Colloidal precipitates could adsorb heavy metallic cations [13].

In the absence of adsorbents, the pH diagram of species distribution of metal ions in aqueous phase can be calculated from a mass balance equation (Eq. (6)) considering the following formation reactions (Eq. (7)):

$$[M]_{\text{tot}} = [M^{2+}] + \sum [M(\text{OH})_i^{2-i}] = [M^{2+}] + \sum K_i [M^{2+}] [\text{OH}^-]^i \quad (6)$$



where K_i is the overall formation constant. Table 1 lists several related values of $\log K_i$ at 25°C and zero ionic strength, where the concentration unit in expressing K_i is in molarity [14].

Fig. 3 shows the calculated results, indicating that free ions M^{2+} are the dominant species at $\text{pH} < 7.3$. On the other hand, the precipitate $\text{Co}(\text{OH})_{2,s}$ and soluble neutral species $\text{Zn}(\text{OH})_2$ would compete to form with free ions between $\text{pH} 7.3$ and 9 at an initial metal

Table 1

The overall formation constants of metals and hydroxide ($\log K_i$) in water at 25°C and zero ionic strength [14]

Metal (M)	$M(\text{OH})^+$	$M(\text{OH})_2$	$M(\text{OH})_3^-$	$M(\text{OH})_4^{2-}$	$M(\text{OH})_{2,s}^a$
Co	4.3	9.2	10.5		15.7
Zn	5.0	11.1	13.6	14.8	15.5

^a Solid or precipitate.

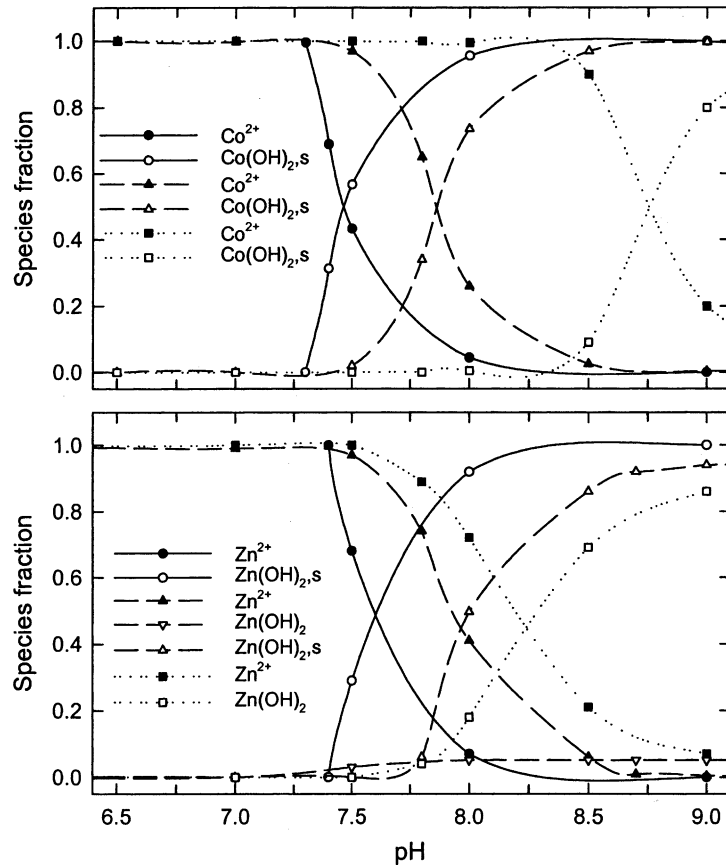


Fig. 3. The pH diagrams of species distribution of Co and Zn in the aqueous phase ($[M]_0 = 6.7$ mg/l (dotted lines), 35 mg/l (dashed line), and 300 mg/l (solid lines)).

concentration of 6.7 mg/l. In this situation, a certain fraction of $\text{Zn}(\text{OH})^+$ (about 0.1) is also present at $\text{pH} > 7.8$. It is hence inferred that the increased removal using Fe_2O_3 and Fe_3O_4 with increasing pH is responsible for their colloidal properties.

Figs. 4 and 5 show the effect of the initial metal concentration on the amounts of Co and Zn adsorbed at pH 7.8. Apparently, Mg pellets have a high removal for Co (94%) over the entire concentration range (0.67–333 mg/l). Although the removal of Co on steel wool and of Zn on Mg pellets and steel wool is still efficient (>94%), the adsorption decreases sharply when the initial metal concentration is higher than 35 mg/l. Hence, Mg pellets and steel wool were chosen to remove metals from dilute solutions in fixed bed experiments. Such a sharp decrease in metal removal at that concentration is probably due to the decrease in the fraction of free ions, Co^{2+} and Zn^{2+} , in aqueous solution as shown in Fig. 3. These results imply that the adsorption of metals on Mg pellets and steel wool occurs by divalent cations, rather than the neutral or negatively charged metal species.

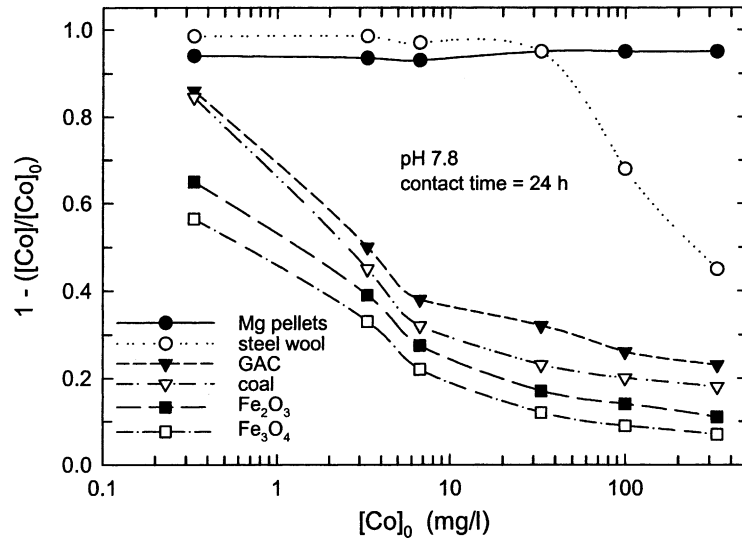


Fig. 4. Effect of initial metal concentration on equilibrium amount of Co adsorbed using various adsorbents (pH 7.8, adsorbent dose = 1.7 g/l).

4.2. Effect of flow rate in fixed bed experiments

Fig. 6 shows the effect of flow rate on the removal of single Co and Zn in fixed beds of steel wool and Mg pellets. The threshold flow rates for Co and Zn are approximately

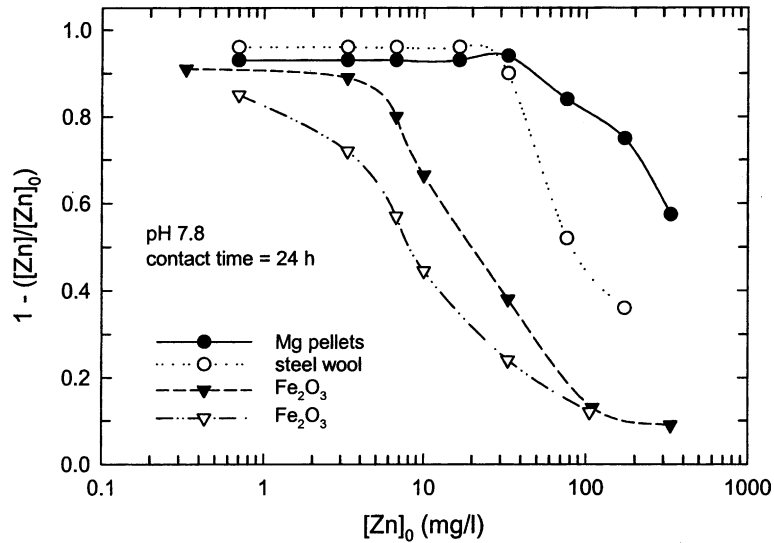


Fig. 5. Effect of initial metal concentration on equilibrium amount of Zn adsorbed using various adsorbents (pH 7.8, adsorbent dose = 1.7 g/l).

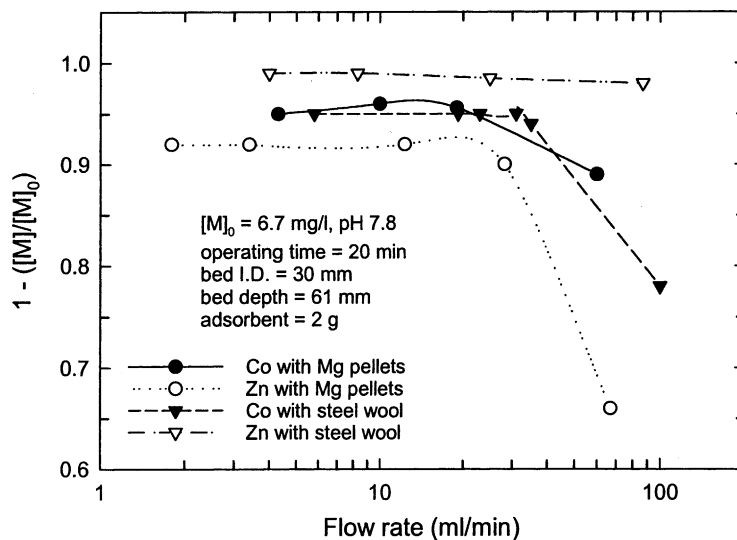


Fig. 6. Effect of flow rate on the amount of metals adsorbed using steel wool and Mg pellets in a fixed bed ($[M]_0 = 6.7 \text{ mg/l}$, inlet pH 7.8).

30 ml/min in the Mg pellet bed under the conditions studied but that effect is less in the case of Co. On the other hand, the removal of Co in the steel wool bed begins to decrease significantly when the flow rate is greater than 50 ml/min. In addition, the flow rate had little effect on the adsorption of Zn in the steel wool bed. Because the equilibrium amounts of single Co and Zn adsorbed on steel wool or Mg pellets are comparable (Figs. 1 and 2), it is likely the adsorption of Co is slightly faster than Zn on Mg pellets, whereas the adsorption of Zn on steel wool is much faster than Co (Fig. 6).

4.3. Modeling of breakthrough curves in fixed bed experiments

According to Eq. (5), a plot of adsorption time, t , versus the logarithm value of $[(M]_0/[M]) - 1]$ yields τ and $1/k$. The results obtained in the Mg pellet bed under various flow rates are shown in Fig. 7. The values of τ and $1/k$ are reported in Table 2. The proposed mass transfer model can be simply established by these two parameters. The calculated and

Table 2
Parameters used in experiments of the adsorption of Co on Mg pellets in a fixed bed^a

Flow rate (ml/min)	τ (min)	k (l/min)	R^2	Q_{Co} (mg/g)
40	103	11.0	0.992	13.7
20	225	32.2	0.987	15.0
13	384	39.7	0.989	16.6
10	542	26.0	0.995	17.9

^a $[Co]_0 = 6.7 \text{ mg/l}$, pH 7.8, adsorbent = 2 g.

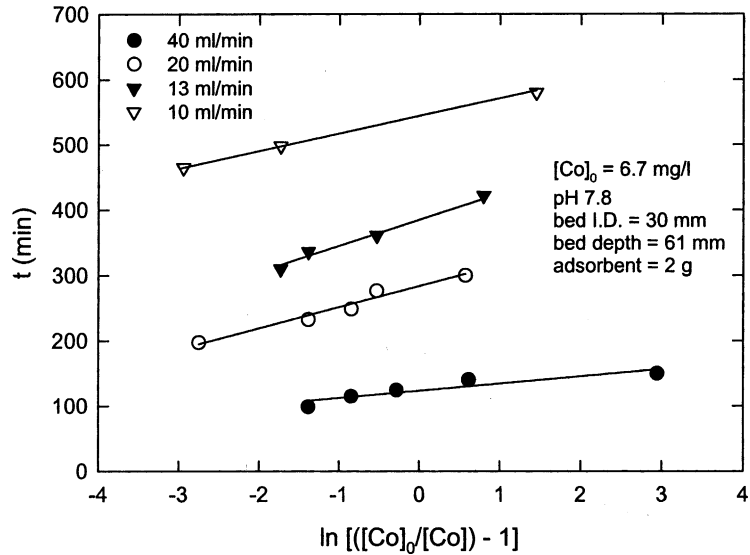


Fig. 7. Linear plots of t vs. $\ln\left(\frac{[Co]_0}{[Co]} - 1\right)$ for the adsorption of Co in the Mg pellet bed ($[M]_0 = 6.7$ mg/l).

measured breakthrough curves are compared in Fig. 8, indicating a quite good agreement in the range of flow rates tested (standard deviation < 6%).

The derivation of Eq. (5) was based on the definition that 50% breakthrough occurs at $t = \tau$ [9]. Thus, the adsorption bed should be completely saturated at $t = 2\tau$. Owing to the symmetrical nature of breakthrough curves, the amount of metals being adsorbed in the Mg

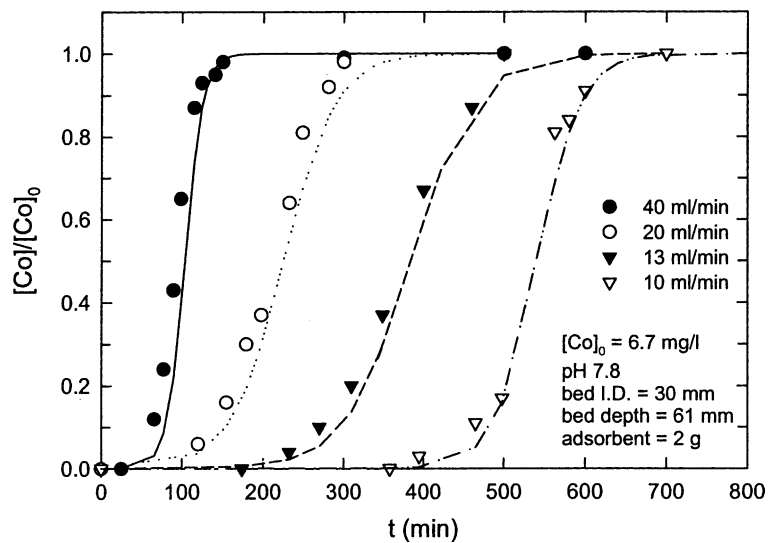


Fig. 8. Effect of flow rate on the breakthrough curves of Co through the Mg pellet bed ($[M]_0 = 6.7$ mg/l).

pellet bed is half of the total metals entering the adsorption bed within 2τ period. Hence, the following equation can be obtained for a given bed [10]:

$$Q_M = \frac{1}{2}[M]_0 F(2\tau) = [M]_0 F\tau \quad (8)$$

This equation permits one to determine adsorption capacity of a given bed Q_M as a function of initial metal concentration $[M]_0$ (mg/l), liquid flow rate F (l/min), and 50% breakthrough time τ (min). As shown in Table 1, τ increases with decreasing the flow rate. On the other hand, the value of k initially increases with increasing flow rate but decreases when the flow rate is greater than 13 ml/min. The present adsorption process is likely controlled by diffusion within aqueous stagnant film at a flow rate below 13 ml/min, and by adsorption reaction when the flow rate is greater than 13 ml/min [9].

The adsorption capacity for Co, Q_{Co} , in the Mg pellet bed increases from 13.7 to 17.9 mg/g when the flow rate decreases from 40 to 10 ml/min (Table 2). This result can possibly be attributed to better contact between stationary adsorbent particles and the flowing solution. This behavior agrees with results reported previously [15,16]. Walker and Weatherley [15] studied the adsorption of acid dyes from industrial wastewater in a fixed bed packed with GAC. They also found that the breakthrough time decreased with increasing the flow rate, and that a lower flow rate produced a longer service time.

For the use of other low-cost metal adsorbents, Bailey et al. [3] have compiled results from the literature results and found that some of the highest adsorption capacities are 1587 mg Pb/g on lignin, 796 mg Pb/g on chitosan, 558 mg Cd/g on chitosan, 92 mg Cr/g on chitosan, and 76 mg Cr/g on peat.

The adsorption capacity of Co on Mg pellets at pH 7.8 was 15.8 mg/g on average, which is also lower than in experiments using waste Fe(III)/Cr(III) hydroxide [5–8]; e.g. 39.0, 40.5, and 47.2 mg Cd/g at 20, 30, and 40 °C, respectively [8]. Such a much low capacity is probably a result of much higher densities and lower specific surface areas of the metal pellets. However, the main advantage of using metal pellets as adsorbents is the fast kinetics (3-min agitation is sufficient to attain adsorption equilibrium). In this regard, the present low-cost adsorbents are particularly suitable for adsorption removal of trace-level heavy metals from waste effluents.

5. Conclusions

The possibility of adsorptive removal of single Co and Zn from effluent by various adsorbents (Fe_2O_3 , Fe_3O_4 , FeS, steel wool, Mg pellets, Cu pellets, Zn pellets, Al pellets, Fe pellets, coal, GAC) has been examined. Batch experiments showed that the removal of Co and Zn using steel wool and Mg pellets were the most effective, and the removal was pH-independent over the entire pH range studied (1.5–9.0). For an adsorbent dose of 1.7 g/l, Mg pellets and steel wool had high removal (>94%) when the initial metal concentration was less than 35 mg/l. However, the amounts of both metals adsorbed using Fe_2O_3 and Fe_3O_4 were small at low solution pH but sharply increased when the pH exceeded a threshold value (3.5 with Fe_2O_3 and 6.2 with Fe_3O_4).

A simplified mass transfer model that only considers two parameters τ and k was proposed to describe breakthrough curves in a fixed bed. The calculated breakthrough results agreed

well with the measured data under the conditions studied (standard deviation < 6%). The adsorption capacity of Co, Q_{Co} , on Mg pellets at pH 7.8 (15.8 mg/g) obtained in this work was lower than the capacity on other low-cost adsorbents such as chitosan, lignin, peat, alginate, and waste Fe(III)/Cr(III) hydroxide. Such a low capacity was probably due to much higher densities and lower surface areas of the metal pellets. The main advantage of using the proposed adsorbents was their comparatively fast kinetics (3-min agitation was enough to attain equilibrium). In summary, these low-cost adsorbents were particularly suitable for removing trace-level heavy metals from waste effluents.

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