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Applications of Inorganic Ion Exchangers: II—Adsorption of Some Heavy Metal Ions from Their Aqueous Waste Solution Using Synthetic Iron(III) Titanate

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Abstract. Adsorption of Zn^{2+} and Cd^{2+} ions from aqueous waste solutions on iron(III) titanate as inorganic ion exchange material was investigated to determine the effect of contact time, pH of solution and the reaction temperatures. Batch kinetic studies were carried out and showed that the time of equilibrium for both Zn^{2+} and Cd^{2+} ions was attained within three hours, and the order of kinetic reaction is the first order reaction. Batch distribution coefficients of Zn^{2+} and Cd^{2+} ions on iron(III) titanate as a function of pH have been studied at 25, 40 and 60 ± 1°C. From the obtained results we found that the K_d values decreased with increasing reaction temperatures. Enthalpy change (ΔH) values for Zn^{2+} and Cd^{2+} ions were found to be -8.19 and -22.49 kJ/mol, respectively. The data of adsorption of Zn^{2+} and Cd^{2+} ions at various concentrations were fitted with the Freundlich isotherm. Finally, separation of the above mentioned cations on iron(III) titanate in a column was performed.

Keywords: adsorption, heavy metals, waste, synthetic, iron(III) titanate

Introduction

Although some of the leading industrialized nations of the world are taking active measures to control environmental damage caused by chemical pollutants, the problem still exists and is becoming even more complicated as time progresses. For example, over five million chemicals are now known to be in common use, and several thousand new ones are synthesized each year. Inevitably some of these chemicals will penetrate into the environment where a certain number of them will eventually affect all forms of life. The actual toxicity of these chemical metals depends on particular metal present, water hardness, pH and synergistic effect of different metals. Ion exchange is a tool used for the removal of hazardous and heavy metals from waste solutions. Among the ion exchange materials used are titanates (Abe et al., 1989; Oliverira and Airoldi, 1993; Lienonen et al., 1994), antimonates (De and Chakraborty, 1982; El-Naggar et al., 1999, 2000, 2000), etc.

In the present work we investigate the adsorption behaviour of Zn^{2+} and Cd^{2+} ions from aqueous waste solutions on iron(III) titanate. One purpose is to explore the usefulness of iron(III) titanate for the preconcentration of some heavy metals from aqueous waste solutions.

Experimental

Chemical Reagents and Apparatus

All chemicals and reagents used in this work were of analytical grade and used without further purification.

Atomic absorption spectrometer, Shimadzu model AA-6701 F, was used for the determination of the metal ion content in the aqueous phase. Microprocessor pH-Meter (HANNA model HI 9321), was used for all pH measurements.

Preparation of Iron(III) Titanate

The iron(III) titanate ion exchanger used in this work was prepared as reported earlier (Abou-Mesalam and El-Naggar, 2002), in a granular form to allow use in the separation process. The empirical formula of iron(III) titanate may be written as $Fe_{1.3}\ TiO_4{\cdot}2H_2O$ (Abou-Mesalam and El-Naggar, 2002).

Batch Kinetic Studies

The time to reach equilibrium was determined by mixing 0.05 g of the exchanger with 5 ml of Zn^{2+} (pH $= 4.15$) or Cd^{2+} (pH $= 4.3$) ion solutions (50 ppm for each) in a shaker thermostat at 25 ± 1°C. After different time intervals the solution was separated and analyzed for Zn^{2+} and Cd^{2+} ions. Adsorption percentage of the exchanger was calculated.

Kinetic analysis of the adsorption process for Zn^{2+} and Cd^{2+} ions on iron(III) titanate was carried out by mixing of the exchanger with 10^{-4} M of the metal ion solution (pH equal to 4.15 and 4.3 for Zn^{2+} and Cd^{2+} ions, respectively) with a V/m ratio of 100 ml/g in a shaker thermostat at 25 ± 1°C. The solution was separated at different time intervals and analyzed to determine the metal ion concentration in solution. The amount adsorbed (Q_t) in mmol of the metal ion per gram of iron(III) titanate was calculated at each time (t) and the relation between $\log(Q_e - Q_t)$ and time was plotted according to Lagergren equation (Mishra and Srinivasu, 1992);

$$\log(Q_e - Q_t) = \log Q_e - (K_1/2.303)t \qquad (1)$$

Where Q_e is the amount adsorbed at equilibrium, Q_t is the amount adsorbed at time (t) and K_1 denotes to the rate constant of the adsorption process.

Batch Adsorption Studies

Distribution Coefficient (K_d). The equilibrations were carried out batch-wise technique. A 0.05 g of iron(III) titanate was mixed with 5 ml of Zn^{2+} or Cd^{2+} ion solutions (50 ppm) at various pH values in a shaker thermostat at 25 ± 1°C. After equilibration the pH and the metal ion content of the supernatant solutions were measured. The distribution coefficient (K_d) was calculated from the following formula;

$$K_d = \frac{\text{Amount of metal ion in the exchanger}}{\text{Amount of metal ion in solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Mass of the exchanger (g)}} \qquad (2)$$

The concentrations of the metal ions in the exchanger were calculated from the differences between the initial and final concentrations in the aqueous phase.

The K_d values of Zn^{2+} and Cd^{2+} ions at pH 7.2 and 5.2, respectively, were measured at different reaction temperatures 25, 40 and 60 ± 1°C to estimate the enthalpy change (ΔH) for the reaction of Zn^{2+} and Cd^{2+} ions with iron(III) titanate.

Effect of Metal Ion Concentrations

The effect of initial concentrations of Zn^{2+} and Cd^{2+} ions on the apparent capacity ($\text{mmol} \cdot g^{-1}$) of iron(III) titanate was determined by mixing of 0.05 g of the exchanger with 5 ml of $ZnCl_2$ (pH $= 4.15$) or $CdCl_2$ (pH $= 4.3$) solutions at different metal ion concentrations. The experiment was carried out in a shaker thermostat at 25 ± 1°C. After three hour (the optimum time to attain equilibrium) the solutions were separated and the metal ion concentrations were measured. The capacity was calculated using the following formula;

$$\text{Capacity} = (C_{\text{initial}} - C_{\text{final}}) \cdot V/m \quad \text{mmol/g} \qquad (3)$$

Where C_{initial} and C_{final} are the initial and final concentrations of the metal ion, V is the solution volume, and m is the mass of the exchanger.

Sorption Isotherm

Sorption isotherms for Zn^{2+} and Cd^{2+} ions on iron(III) titanate were determined over the concentration range 10^{-4} to 5×10^{-2} M at pH $= 5$ and at a V/m ratio of 100 ml/g. The experiments were carried out by mixing 0.05 g of the exchanger with 5 ml of the desired metal solutions in a shaker thermostat at 25 ± 1°C. The equilibrium concentration (C) and the amount uptake (W/m) were calculated as follows:

$$W/m = \text{Uptake} \times C_o \times V/m \qquad (4)$$

$$C = C_o\{1 - (\%\text{Uptake}/100)\} \qquad (5)$$

Where % uptake is the percentage of the amount of metal ion in the exchanger after a certain time, *t*, to the initial amount of the metal ion in solution, and C_o is the initial concentration of the metal ion. Plots of *C* against *C/W* or log *C* against log *W/m* were performed to obtain the required isotherms.

Column Experiments

Iron(III) titanate was tested with zinc and cadmium solutions to assess metal sorption performance and its selectivity towards the studied metal ions. A sample of 0.5 g of iron(III) titanate (particle diameter 0.212 mm) was packed into a glass column with 1.8 cm length and 0.6 cm internal diameter. Feed containing a mixture of Zn^{2+} and Cd^{2+} ions (50 ppm for each), at a pH of 4, was passed through the column from the top to bottom at a flow rate of 1 ml/minute. The effluent from the column was collected every 10 minutes and analyzed to determine the metal ion concentration. This was continued until the concentration of metal leaving the column was very close to that of the feed.

Results and Discussion

Batch Kinetic Studies

The data shown in Fig. 1 shows that the equilibrium for the exchange of both Zn^{2+} and Cd^{2+} ions on iron(III) titanate was attained within three hours.

In order to determine if intraparticle diffusion is the sole rate limiting mechanism for adsorption of Zn^{2+} and Cd^{2+} ions on iron(III) titanate, the amount adsorbed (mmol/g) was plotted against the square root of time, as shown in Fig. 2. Weber and Morris (1963) stated that if intraparticle diffusion is the sole rate-controlling factor, the amount adsorbed of the adsorbate varies proportionately with the square root of time. Since the plots obtained for Zn^{2+} and Cd^{2+} ions do not pass through the origin, intraparticle diffusion may not be the sole rate-limiting factor (Weber and Morris, 1963). The order of reaction for both Zn^{2+} and Cd^{2+} ions with iron(III) titanate was determined in this work using Lagergren equation (Mishra and Srinivasu, 1992). Figure 3 shows the linearity relationship between $\log(Q_e - Q_t)$ and time according to the Lagergren equation, which confirms the first order kinetics for both Zn^{2+} and Cd^{2+} ions on iron(III) titanate.

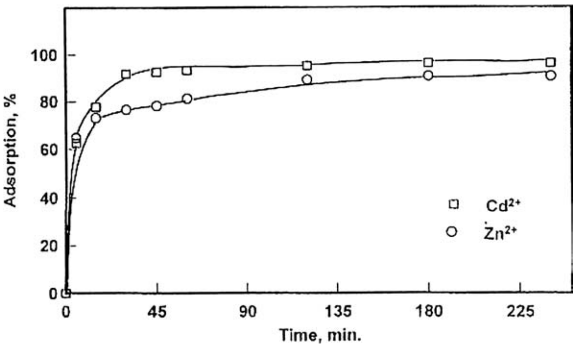

Figure 1. Adsorption % against time for Zn^{2+} (pH = 4.15) and Cd^{2+} (pH = 4.3) ions on iron(III) titanate at 25 ± 1°C.

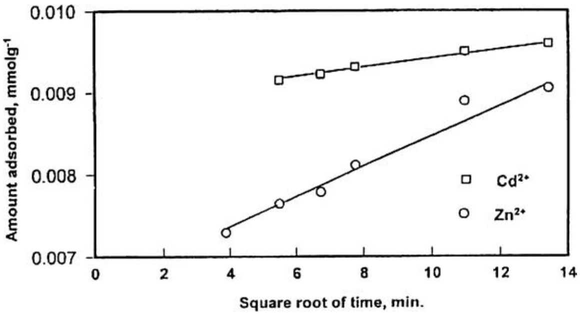

Figure 2. Plots of amount adsorbed versus square root of time for the adsorption of Zn^{2+} (pH = 4.15) and Cd^{2+} (pH = 4.3) ions on iron(III) titanate at 25 ± 1°C.

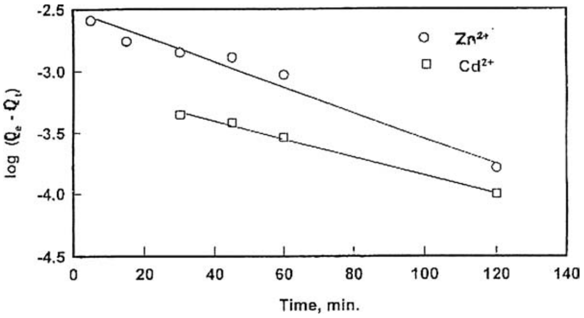

Figure 3. Plots of $\log(Q_e - Q_t)$ versus time for the adsorption of Zn^{2+} (pH = 4.15) and Cd^{2+} (pH = 4.3) ions on iron(III) titanate at 25 ± 1°C.

Batch Adsorption Studies

Distribution Coefficient Values (K_d). The K_d values of Zn^{2+} and Cd^{2+} ions on iron(III) titanate as a function of pH of solution at constant concentration of the

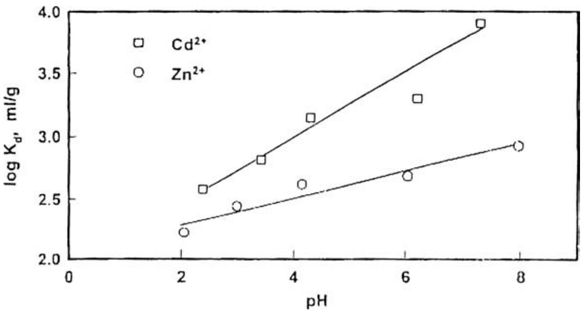

Figure 4. Variation of log K_d versus pH for adsorption of Zn^{2+} and Cd^{2+} ions on iron(III) titanate at 25 ± 1°C.

cations in solution are represented in Fig. 4. A linear relation between log K_d and pH was observed, as predicted from the following:

When the simple ion exchange proceeds by the following reaction

$$n\bar{H}^{+} + M^{n+} \longleftrightarrow \bar{M}^{n+} + n\mathrm{H}^{+} \tag{6}$$

in a sufficiently dilute solution, where the activity coefficient may be neglected, the selectivity coefficient can be defined by the following equation (Helffrich, 1962);

$$K_H^M = \frac{[\bar{M}^{n+}][H^+]}{[\bar{H}^+]^n[M^{n+}]} \tag{7}$$

where $[\bar{M}^{n+}]$ and $[\bar{H}^+]$ denote to the concentrations of M^{n+} and H^+ ions in the exchanger, respectively, and $[M^{n+}]$ and $[H^+]$ are their concentrations in solution. Since the K_d value is the ratio between the metal ion concentration in the exchanger and in the solution, then

$$K_H^M = K_d\frac{[H^+]^n}{[\bar{H}^+]^n} \tag{8}$$

or

$$K_d = K_H^M\frac{[\bar{H}^+]^n}{[H^+]^n} \tag{9}$$

by taking the logarithm of both sides

$$\log K_d = \log K_H^M[\bar{H}^+]^n - n\log[H^+] \tag{10}$$

When $[\bar{M}^{n+}] < [\bar{H}^+]$ and $[M^{n+}] < [H^+]$, the magnitude $K_H^M\ [\bar{H}^+]^n$ is considered constant, thus Eq. (10) can be reduced to

$$\log K_d = C + n\,\mathrm{pH} \tag{11}$$

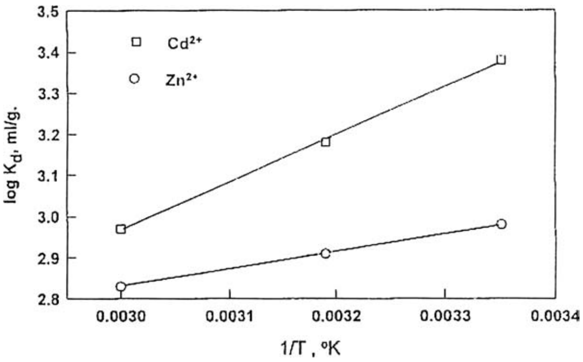

Figure 5. Variation of log K_d with 1/T for the adsorption of Zn^{2+} (pH = 7.2) and Cd^{2+} (pH = 5.2) ions on iron (III) titanate.

Which implies that a plot of log K_d versus pH should be linear with a slope (n). Figure 4 shows the dependency of K_d values of $Zn^{2+}$and Cd^{2+} ions on the pH of the solution with slopes equal to 0.13 and 0.26, respectively. That deviation from unity implies that the exchange reaction is non-ideal. The non-ideality may be due to the presence of an other rate-limiting mechanism besides the ion exchange mechanism, such as the formation of covalent bonds between the metal ions and the exchanger, which could be related to the ionic potential of the cations.

The enthalpy change for the reaction of Zn^{2+} and Cd^{2+} ions with iron(III) titanate can be calculated by determining the K_d values at different reaction temperatures according to the equation;

$$\Delta H = -2.303R\frac{d\log K_d}{d(1/T)} \tag{12}$$

when log K_d values are plotted against $1/T$, straight lines were obtained. Figure 5 shows the dependence of log K_d on $1/T$ is linear over a wide range of temperature (25 to 60 ± 1°C), and log K_d decreases with increasing the reaction temperature. From the computed slopes, the enthalpy change (ΔH) for both Zn^{2+} and Cd^{2+} ions are −8.19 and −22.49 kJ/mol, respectively. So the exchange process is exothermic. That observation is supported by other experimental results as adsorption decreases at higher reaction temperatures (Helffrich, 1962).

Apparent Capacity Measurements

The capacities of iron(III) titanate for both Zn^{2+} and Cd^{2+} ions were determined at different metal ion concentrations and the results were represented in

Table 1. Variation of apparent capacity of iron(III) titanate with zinc (pH = 4.15) and cadmium (pH = 4.3) concentrations at 25 ± 1°C.

	Capacity ($mmol \cdot g^{-1}$)	
Metal concentration (M)	Zn^{2+}	Cd^{2+}
5×10^{-2}	4.70	3.10
10^{-2}	0.95	0.82
5×10^{-3}	0.48	0.44
10^{-3}	0.095	0.09
5×10^{-4}	0.05	0.05
10^{-4}	0.01	0.01

Table 1. The values in Table 1 show that the capacities of iron(III) titanate for both Zn^{2+} and Cd^{2+} ions increase with increasing metal ion concentrations. Table 1 also shows that the capacity of iron(III) titanate for Zn^{2+} ion are higher than Cd^{2+} ion which may be attributed to the fact that both cations are adsorbed in a dehydrated state, whereas the ionic radius of Zn^{2+} ion is smaller than Cd^{2+} ion in the dehydrated state. The small radius of dehydrated Zn^{2+} ion increases the mobility and the packing density of the Zn^{2+} ion compared to the Cd^{2+} ion, which facilitates the greater adsorption of Zn^{2+} ion on iron(III) titanate. Similar results have been reported by El-Naggar et al. (1999) in the adsorption studies of $Cs^{+}$and Na^{+} ions on cerium(IV) and tin(IV) antimonates.

Sorption Isotherm

The adsorption of Zn^{2+} and Cd^{2+} ions on iron(III) titanate over the entire concentration range 5×10^{-2} to 10^{-4} M were fitted by the Freundlich isotherm equation:

$$\log W/m = \log K + 1/n \log C \tag{13}$$

where

W/m: is the amount adsorbed at equilibrium, K and $1/n$ are Freundlich constants that measure the adsorption capacity and the adsorption intensity of the adsorbent, respectively (computed from intercept and slope of the linear relation obtained), and

C: is the equilibrium concentration that can be calculated using Eq. (5).

As seen in Fig. 6, a linear relationship was obtained from the plots of log W/m for both Zn^{2+} and Cd^{2+} ions on iron(III) titanate against log C. That indicates that both Zn^{2+} and Cd^{2+} ions are physically adsorbed on iron(III) titanate. The values of K were found to be 3.98×10^{-3} and 7.97×10^{-3} mol/g $(L/mol)^{1/n}$ for Zn^{2+} and Cd^{2+} ions, respectively. The numerical values of 1/n for both Zn^{2+} and Cd^{2+} ions were found to be 0.89 and 0.6, respectively. According to the statistical theory of adsorption (Clark, 1970), when the value of $1/n$ in the adsorption isotherm is less than unity, it implies heterogeneous surface structure with minimum interactions between the adsorbed atoms.

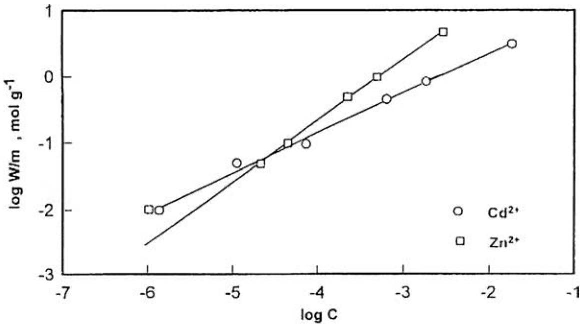

Figure 6. Freundlich adsorption isotherms for Zn^{2+} and Cd^{2+} ions on iron(III) titanate at pH = 5; 25 ± 1°C.

Column Chromatography

As the application studies and based on the granular nature of the synthesized iron(III) titanate and the data obtained from the distribution coefficients of Zn^{2+} and Cd^{2+} ions on iron(III) titanate, column experiments were carried out to investigate the possible removal of these hazardous cations from their aqueous waste solution at pH = 4. Figure 7 shows the breakthrough curves for a mixture of Zn^{2+} and Cd^{2+} ions (50 ppm) at pH = 4 on iron(III) titanate column (particle diameter 0.212 mm). Each breakthrough curve depicts the percent concentration of the respective metal ion in the effluent to the feed solution (C/Co, %) versus effluent volume (ml). The data in Fig. 7 can be used to calculate the breakthrough capacity for both Zn^{2+} and Cd^{2+} ions using the following formula;

$$Q = \left\{ V_{(50\%)}/m \right\} \times C_o \tag{14}$$

where

Q: is the breakthrough capacity,
V: is the volume of the effluent,

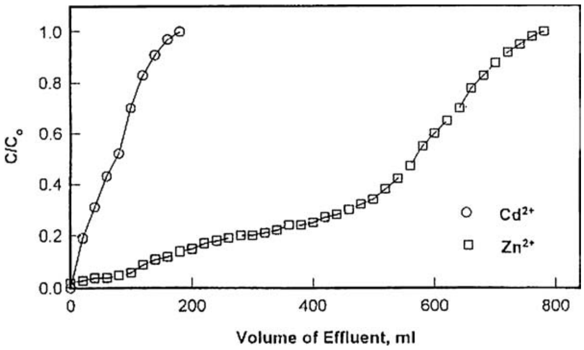

Figure 7. Breakthrough curves for Zn^{2+} and Cd^{2+} ions on iron(III) titanate column (i.d. = 0.6 cm and length = 1.8 cm) with particle diameter 0.212 mm at pH = 4; 25 ± 1°C.

m: is the mass of the dry solid, and
C_o: is the initial concentration of the metal ion.

The results indicated that the breakthrough capacities of iron(III) titanate for both Zn^{2+} and Cd^{2+} ions are 0.9 and 0.06 mmol/g, respectively. These results are higher than those obtained from the batch technique. This may be due to the arrangement of the exchanger in the column in a number of equal unites called theoretical plates according to the plate theory (Qureshi and Varshney, 1991). Each theoretical plate is filled with the loaded cations in arranged manner so the number of mile-mole of the loaded cations per gram of iron(III) titanate is higher than those obtained from the batch technique. Also the results of the breakthrough capacities of iron(III) titanate for Zn^{2+} and Cd^{2+} ions show the high selectivity of iron(III) titanate for the adsorption of Zn^{2+} ion than Cd^{2+} ion from their aqueous waste solutions.

Conclusion

From all the above mentioned data we can conclude that; iron(III) titanate is an inorganic ion exchanger suitable for the removal of some heavy metals, such as Zn^{2+} and Cd^{2+} ions from their aqueous waste solutions in the pH range 2 to 8. Both Zn^{2+} and Cd^{2+} ions are physically adsorbed on iron(III) titanate and fitted to the Freundlich isotherm. Finally, based on the statistically adsorption theory the adsorption surface of iron(III) titanate is a heterogeneous type.

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