ADSORPTION AND DESORPTION OF Cd^{2+} IONS ON ION-EXCHANGE RESIN USING SUB-CRITICAL WATER AND CARBON DIOXIDE

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A study of regeneration of the ion exchange resins using a sub-critical mixture of CO_2-H_2O solution was reported. The experimental data were obtained by measuring the outlet concentration of ions Cd^{2+} eluated from a column packed with a commercial ion exchange resin Amberlite IRC-86 until the effluent reached the input concentration. The adsorption isotherm was also reported. The correlation of the experimental data indicated that the Langmuir model can be applied in this sorbent system. After adsorption process, the resin bed was desorbed in the same apparatus, but using the countercurrent process. The results indicated that the resin can be fully regenerated, with desorption efficiency above 99 %. However, The adsorption and respective desorption of metal ions was strongly dependent on the feed concentration. Lean feed is found to be better for both adsorption and desorption processes.

INTRODUCTION

The presence of heavy metals in water and wastewater is an issue of increasing importance because of their hazardous properties to human beings, such as toxicity, persistence, bioaccumulation, and carcinogenicity [1]. The most widely used process to remove heavy metals is generally accomplished by the precipitation process. However, the precipitation process usually results in contaminated sludge that has to be landfilled, which later makes groundwater polluted [2]. Ion exchange technology has been used commercially on a worldwide basis for almost a century, and practically all industries and homes are dependent upon this technology either directly or indirectly. The most important property of ion exchange resins is that they can be regenerated and therefore be reused. The supercritical fluid technology has received widespread attention over the past years. The applications of this technology in different areas have been reviewed in detail by Perrut [3], Chordia and Robey[4], Marr and Gamse [5]. One of its application is to regenerate adsorbents. Picht et al. [6] studied the regeneration of five adsorbents loaded with acetic acid, phenol and alachlor. Tan and Liu [7,8] investigated the desorption of ethyl acetate and a binary mixture containing benzene and toluene from activated carbon by supercritical CO_2. A study of the regeneration of the sodium form of some carboxylic cation exchange resins using pressurized CO_2 solutions was carried out by Kunin and Vassiliou [9] and demonstrates that the regeneration efficiency of carbonic acid depends upon the acidity of the resin. The CARIX process represent a example in treatment of drinking water with ion exchange resins, where the exhausted resins are regenerated simultaneously by CO_2 and water. In the pilot scale the CARIX process has successfully been applied to the combined removal of hardness, sulfate, and nitrate [10]. In this work, sub-critical water and carbon dioxide has been applied as an alternative method to investigate the possibility of recovering heavy metals, particularly Cd^{2+} from loaded ion exchangers resins. Desorption experiments have been carried out in a supercritical pilot plant at 250 bar, temperature of 35 °C.

I – MATERIALS AND METHODS

1 MATERIALS

An anion exchange resin Amberlite IRA-67 in the free base form and the cation exchange resins Amberlite IRC-86 in the H-form were tested in this study, supplied by Aldrich. The column experiments were performed on ion exchange resin with particle size 16-50 mesh. Analytical grade reagent $Cd(NO_3)_2$ [Merck] were used. Solutions of approximately 100 mg/L were prepared using distilled water as a solvent.

2 ADSORBENT PREPARATION

In order to improve the adsorption process, the anion exchange resin Amberlite IRA-67 was converted to the bicarbonate form by activation with CO_2-H_2O mixture at 25 MPA and 308 K. In principle, the reaction is [11]:

$$[R-N] + H_2O + CO_2 \rightarrow [R-NH]HCO_3^- \qquad (1)$$

II - EXPERIMENTAL PROCEDURES

After activation, the anion exchange resin Amberlite IRA-67 in the HCO_3^- form was used in the same SS column(Autoclave Engineers) with 17.2 mm inner diameter and 486 mm length. The cation exchange resin Amberlite IRC-86 was packed in other SS column(Autoclave Engineers) with 14 mm inner diameter and 490 mm length (Fig. 1).
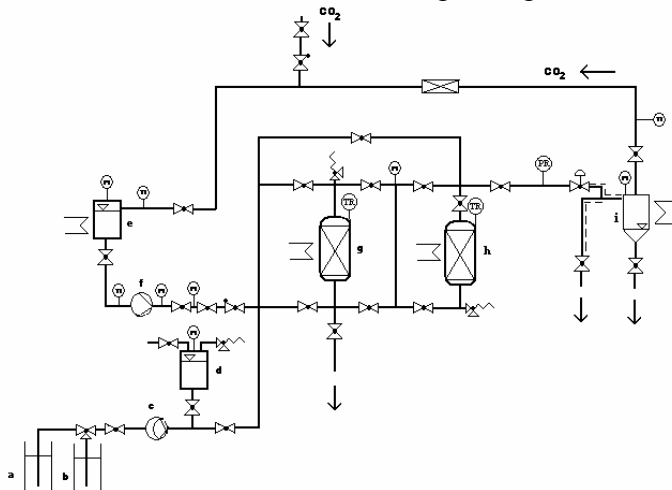
Figure 1: The experimental set-up (a,b: water and metal solution vessel; c: high pressure membrane pump; d: pulsation damper; e: condensation vessel; f: piston pump; g: cation exchanger column; h: anion exchanger column; i: separation vessel.

Columns were operated in the down-flow mode at room pressure in the adsorption experiments. First, the ion exchange columns were washed with distilled water and after this, the feeding metal solution was pumped through the column by a Lewa model EK1 membrane pump . The experiments were carried out at constant temperature and effluent samples were collected, and than stored for metal analysis. Metal concentration was measured using a atomic absorption spectrophotometer (Perkin-Elmer Optima 2000 DV OES/ICP) in the Central

Laboratory at the TUHH. After the adsorption experiment, the direction of the flux (H_2O-CO_2) through the columns contained loaded cation and anion resins was invert in order to make the desorption experiment in the same apparatus. The carbon dioxide delivered by the CO_2 reservoir passed through a cooler to be pumped as a liquid into the system, at a desired pressure, until a point whereas was mixed with distilled water at the same pressure to feed the system. In the columns, the mixture of H_2O-CO_2 at a prescribed state condition (P and T) extracts the heavy metal from the adsorbent particles. The solution H_2O-CO_2 + heavy metal was separated by pressure reduction, and sample were collected to analyze the Cd^{2+} concentration. Table 1 summarizes the experimental conditions at each column run.

Table 1: Experimental conditions.

Adsorption Experiment	Flow rate [L/h]	C_0 [mg/L]	Desorption Experiment	H_2O Flow rate[L/h]	CO_2 Flow rate[g/min]
ISOIa	**14.59**	**44.5**	**ISOId**	**2.71**	**9.93**
ISOIIa	**15.31**	**147**	**ISOIId**	**2.95**	**18.82**
ISOIIIa	**13.82**	**204**	**ISOIIId**	**2.55**	**23.86**
ISOIVa	**15.79**	**21.8**	**ISOIVd**	**---**	**---**
ISOVa	**15.66**	**297**	**ISOVd**	**2.57**	**18.49**

As described in table above, the desorption experiment ISOIVd had presented problems and was not possible to realize, therefore it was discarded of the calculus.

III - RESULTS AND DISCUSSION

Figures 2-5 show the adsorption-desorption curves for Cd^{2+} at different initial concentration. Figure 2 gives the adsorption and desorption curve at a lower Cd^{2+} concentration in the feed solution (44.5 mg/L). The breakpoint occurred at approximately 500 bed volumes, where the resin bed could adsorb 2380.60 mg of Cadmium. Approximately two thousand bed volume of feed solution were required for complete saturation. The capacity of the resin bed at complete saturation was 52.24 mg/g of resin. For the regeneration of the resin, approximately 400 bed volumes was required to regenerate the bed, showing that the desorption rate was fastest that adsorption rate.
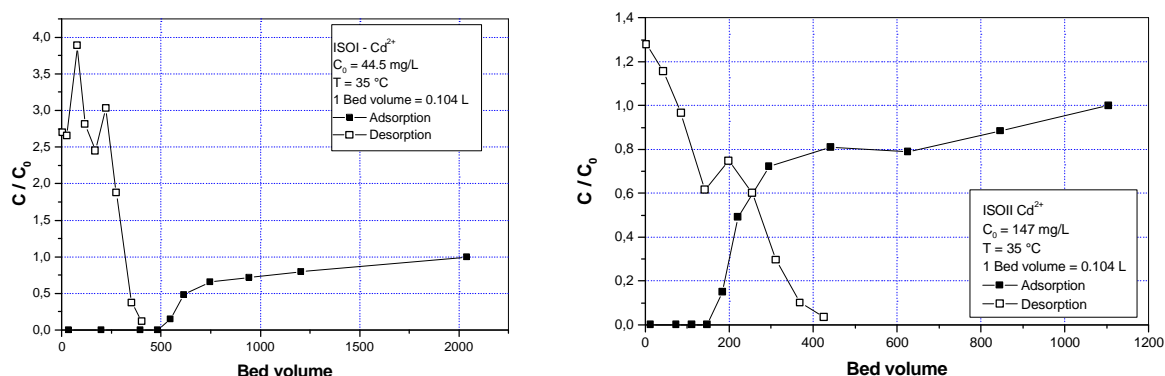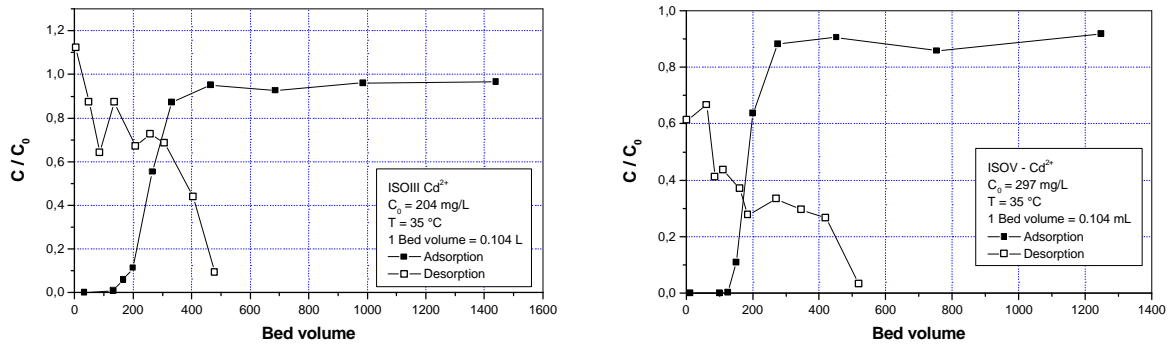

Figure 2: Adsorption and desorption breakthrough curves for C_0 = 44.5 and 147mg/L.

The adsorption studies with the feed concentration of metal at 147 mg/L is showed in Figure 2. At the breakpoint, approximately 150 bed volumes, the resin bed had adsorbed a total of 2250.57 mg of Cd^{2+}. This amount correspond to the loading capacity of 29.04 mg/g resin. On

complete saturation of the bed, for which approximately 1100 bed volumes of the feed solution were required, the bed showed the capacity of 68.17 mg/g resin. Figure 2 also shows the desorption curve of the Cd^{2+} when the mixture of H_2O-CO_2 was passed through of the saturated column. Approximately 420 bed volumes were required for regeneration of resin. However, the complete regeneration was not reached.

Figure 3 shows the adsorption studies with a feed metal concentration of 204 mg/L. The breakpoint occurred at approximately 130 bed volumes, where the resin bed had adsorbed 2793.02 mg of Cd^{2+}. Approximately 500 bed volumes of regenerant were required for complete regeneration of the resin bed. No significant difference was observed in adsorption and desorption rates.

Figure 3: Adsorption and desorption breakthrough curves for C_0 = 204 and 297 mg/L.

In Fig. 3 one can see that no significant difference was observed in the adsorption and desorption breakpoint value when C_0 = 297 mg/L, equal to that described in previous run ISOIII. Despite the desorption process presenting not total efficiency of resin regeneration, the rate of desorption was higher than the adsorption process, with approximately 500 bed volumes, here also equal to the described in run ISOIII.

The total amounts of Cd^{2+} recovered from the ion exchange resin obtained by integrating the elution curves were compared with the initial amount of Cd^{2+} loaded onto the resin in Table 2. It was found that the desorption efficiency was greater than 89% for all process. However, the bed volumes of the eluent differed greatly, depending on the initial loading concentration.

Table 2: Desorption efficiency at different feed concentration.

| Initial Cd^{2+} concentration [mg/L]	Amount Cadmium loaded [mg]	Amount Cadmium desorbed [mg]	Recovery [%]
44.5	4048.6	4043.0	99.86
147	5283.17	3921.09	74.22
204	6020.2	6020.2	100
297	6035.7	5414.85	89.71

The extent of adsorption in column experiment can be see from adsorption isotherm applied to the column exhaustion point. The metal retained in column has been calculated from the area above the breakthrough curve up to the experimental column end point. For describe mathematically the adsorption isotherm, the Langmuir expression isotherm was tested. The Langmuir isotherm is still the simplest and most useful isotherm for describing both physical

and chemical adsorption. The Langmuir model could be applied in this system and can be described by the equation:

$$q = \frac{q_{MAX} C_{eq}}{K_d + C_{eq}} \tag{2}$$

where C_{eq} is the equilibrium concentration of adsorbate in solution; q is the solid-phase concentration of the adsorbed ions; q_{MAX} is the maximum adsorption capacity of the adsorbed; and K_d is the Langmuir constant. The corresponding calculated adsorption isotherm is shown in Fig. 4. The maximum capacity (q_{MAX}) data for Cd^{2+} adsorption was obtained from experimental data. The correlation coefficient (R^2) was 0.98675, indicating that the Langmuir model can be applied in this sorbent system. The maximum adsorption capacity (q_{MAX}) was 84.96 mg/g and the K_d value was 28.14 mg/L.

Modeling of the metal desorption was carried out successfully as an extraction process. For these purpose, a VTII-Model that is applied for the extraction from solids using supercritical solvents, was available in this work.
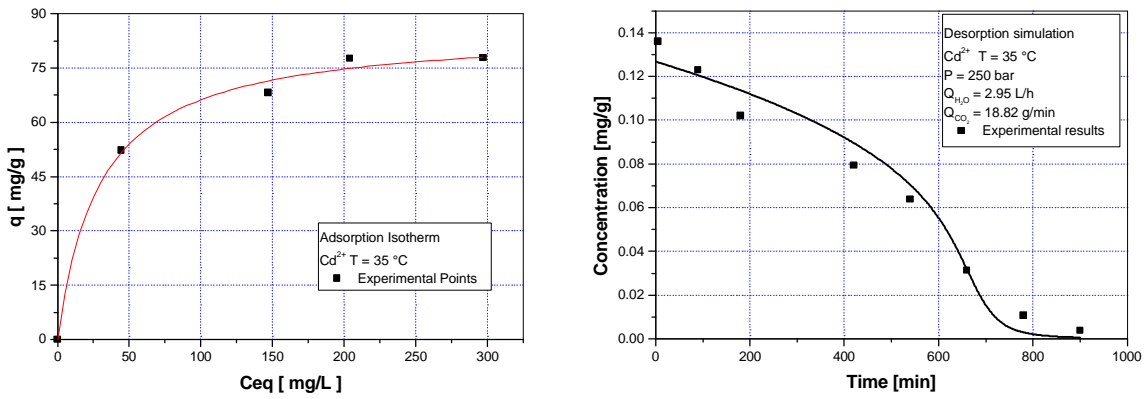
Figure 4: Equilibrium (Langmuir isotherm) and kinetic (VTII) models simulation.

The four equations of the model are given below:

$$\frac{\partial c_F}{\partial t} = D_{ax} \cdot \frac{\partial^2 c_F(z)}{\partial z^2} - \frac{u_z}{\varepsilon} \cdot \frac{\partial c_F(z)}{\partial z} - \frac{1-\varepsilon}{\varepsilon} \cdot \frac{\partial \overline{c}(z)}{\partial t} \qquad \frac{\partial \overline{c}(z)}{\partial t} = a \cdot k_{oG} \left(c_F(z) - \overline{c}_S(z) \cdot \frac{K(\overline{c})}{r_{solid}} \right) \tag{3}$$

$$K(\overline{c}_S) = k_1 \cdot \overline{c}_S^{-k_2} \qquad\qquad \frac{b_F}{k_{oG}} = 1 + \frac{Bi \cdot K(\overline{c}_S)}{6} \tag{4}$$

with, $\overline{C}_S$ = mean concentration of extract components in the solid phase; C_F = concentration of extract in the fluid; D_{AX} = axial dispersion coefficient; u_Z = void volume linear velocity of solvent; $K(\overline{C}_S)$ = equilibrium distribution coefficient between solid and fluid phase; D_{es} = effective diffusion coefficient in the solid phase; k_{oG} = overall mass transfer coefficient in the solid phase; z = coordinate in axial in axial direction; e = void volume fraction (porosity of the fixed bed); t = time of extraction; a = specific surface of solid phase (mass transferring surface area); r_{solid} = density of solid; k_1, k_2 = coefficients of the sorption isotherm

(Freundlich-isotherm); $\boldsymbol{b}_F$ = mass transfer coefficient for the fluid phase. Experimental desorption curve have been represented by this model by fitting the kinetic coefficients ($\boldsymbol{b}_F, D_{es}, D_{AX}$) to the experimental curve obtained from a desorption experiment. An example is presented in Fig. 4. The experimental and calculated desorption curves are compared for cation exchange resin Amberlite IRC-86; the coincidence is sufficient.

CONCLUSION

In this study, the regeneration of the commercial ion exchange resin IRC-86 loaded with Cd^{2+} by using the mixture of H_2O-CO_2 was investigated. Results from the columns studies established that the removal of Cd^{2+} can be successfully carried out by adsorption on ion exchange resin Amberlite IRC-86. The sorption of metal ions was strongly dependent on the feed concentration and lean feed is found to be better for metal recovery. From this study, it can be concluded that the Langmuir model leads to a better correlation of the data, with maximum adsorption capacity to be 84.96 mg/g. The obtained fitting between experimental and the kinetic VTII extraction model points have showed their adequacy for ion exchange system. The effect of cadmium feed concentration on the resin regeneration was also studied. The results indicated that the resin can be fully regenerated, with desorption efficiency above 99 %. However, here again lean feed in adsorption experiment is found to be better for desorption of Cd^{2+}, because little bed volumes was required.

REFERENCES:

[1] BISKUP, B.; SUBOTIC, B. Separation Science Technology, 35(14), **2000**, p. 2311.

[2] TAI, C. Y.; YOU, G. S.; CHEN, S. L. Journal of Supercritical Fluids, Vol. 18, **2000**, p. 201.

[3] PERRUT, M. Proc. 5th Italian Conference on Supercritical Fluids and their Applications, Garda, Italy, **1999**, p. 1.

[4]CHORDIA, L.; ROBEY, R. Proc. 5th International Symposium on Supercritical Fluids, Atlanta, USA, **2000**.

[5] MARR, R.; GAMSE, T. Chemical Engineering and Processing, Vol. 39, **2000**, p. 19.

[6] PICHT, R. D.; DILLMAN, T. R.; BURKE, D. J.; DEFILIPPI, R. P. AiChE – Symposium Series. American Institute of Chemical Engineers, Nr. 29, Vol. 78, **1982**, p. 136.

[7] TAN, C. S.; LIOU, D. C. Ind. Eng. Chem. Res., Vol. 27, **1988**, p. 988.

[8] TAN, C. S.; LIOU, D. C. Ind. Eng. Chem. Res., Vol.28, **1989**, p. 1222.

[9] KUNIN, R.; VASSILIOU, B. Industrial & Engineering Chemistry, 2(1), **1963**, p.1.

[10] HÖLL, W.; FLEMMING, H.C. Ion Exchanges. Konrad Dorfner ed., Berlin, **1991**, p. 841.

[11] BRUNNER, R.; VASSILIOU, B. Mitteilung VGB-Speisewassertagung, **1968**, p. 61.