PURIFICATION OF $CaCl_2$ SOLUTIONS USING PUROLITE S930 RESIN DYNAMIC STUDIES

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Abstract: *Resin Purolite S930 is used with numerous applications in refining salt solutions concerning transition metals. This work presents the influence of experimental conditions(?) to remove Fe(II) from 34% $CaCl_2$ solutions using chelating resin Purolite S930 in dynamic regime and also the experimental conditions about desorbtion efficiency. The resuls show that under circumstances ($T=22^0C$, volume of resin = 10,2 ml, layer heihgt=13 cm, pH=2.3), usable breakthrough capacity decrease with the increasing of feeding flow and increasing of the concentration of Fe(II) in feeding solution. The volume of refined solution decreases with the increasing of Fe(II) concentration in feeding solution. Usable capacity for sorbtion in dynamic regime is 197 mg Fe(II)/g. Desorbtion effiency increase with height of resin bad and HCl concentration. Increasing the concentration of HCl from 2N to 10% and resin dose from 2 grames to 4 grames desorbtion effiency increases from 50 to 520 times.*

Keywords: *dynamic, Purolite, capacity, desorbtion*

1. Introduction

One of the most used techniques to remove heavy metals from solutions is based on ion exchange process. There were tested different typs of polymers who operate in different conditions to obtain maximum sorption capacity [1]. Resin Purolite S930 is used with numerous applications in refining the salt solutions concerning transition metals, for purification of organic and anorganic chemical solutions from heavy metals [2]. The percent of Fe(II) removal from 34% $CaCl_2$ solution by ion exchange in static regime depends on process variables, such as initial solution pH, initial metal ion concentration, metal/resin ratio, contact time and temperature [3].
In this study, the Purolite S930 resin with iminodiacetic acid (IDA) functional groups was used to remove Fe(II) ions from synthetic 34% calcium chloride solution, in dynamic regime. In literature technical data, the value of capacity for different types of resins is around 200 mg/g [4].

Table 1.
Capacity for different types of resins

Metal	Resin	Capacity (mg/g)	Reference
Fe(III)	Amberlite IRC-50	200	P.A. Riveros 2004 [7]
Fe(III)	Amberlite IRC-76	235.2	
Fe(III)	Dowex MAC-3	182.9	
Fe(III)	Duolite C-433	231.5	
Fe(III)	Duolite C-436	216.5	
Fe(III)	Amberlite IRC-86	225.9	

2. Materials and methods

2.1. Materials. The chelating resin used in the experiments was S930 obtained from Purolite International Limited (Hounslow. UK). The main physical and chemical properties of the resin are presented in table 2.

Table 2.
Characteristic proprieties of the chelating resin

Polymer matrix structure	**Macroporous styrene divinylbenzene**
Functional groups	Iminodiacetic acid
Ionic Form (as shipped)	Na^+
pH range (operating): H^+ form; Na^+ form	2 - 6; 6 - 11
Maximum operating temperature	70ºC
Particle size range	+ 1.0mm < 10%. - 0.3mm < 1%
Total exchange capacity	≥ 1.9 meq/mL

***** Manufacturer supplied.

The conversion of the sodium form of the resin into hydrogen form was made with 10% HCl solution. followed by washing with distilled water until the pH of the effluent dropped to neutrality. Accordingly to the manufacturer supplied. the resin has been dried using an oven at 60 ºC. to avoid thermal destruction of functional groups.
The calcium chloride 34 % solution with iron was prepared using $CaCl_2$ analytical-reagent grade and distilled water. In this solution was added 2g/L Fe(II) solution to obtain 100 - 200 mg Fe(II)/L in 34% $CaCl_2$ solution. The stock solution of iron (2g Fe(II)/L) was prepared from analytical-reagent grade iron sulphate ($FeSO_4 \cdot 7H_2O$) in distilled water and hydrochloric acid. analytical-reagent grade.

2.2. Sorbtion experiments. To find exchange capacity in dynamic regime was performed a classic installation [5]. like in figure 1. formed by an glass column (6) filled with exchange resin. solution storage tank (1). thermostat (8). magnetic stirrer (4). flowmeter (5) intermediate vessel for feeding. overflow (2). intermediate vessel for collect tap (3). eluate collection vessel (7). control valve (9.10). The values of column parameters are predicted as a function of flow rate and bed hight. In all the studies was used the same column (10 mm inner diameter).
Synthetic calcium chloride solution containing Fe(II) in controlled concentration and maintained under stirring was fed from the top of the column. Flow was adjusted with control valves and intermediate vessels wich helps to maintain a constant liquid level in the column resin.

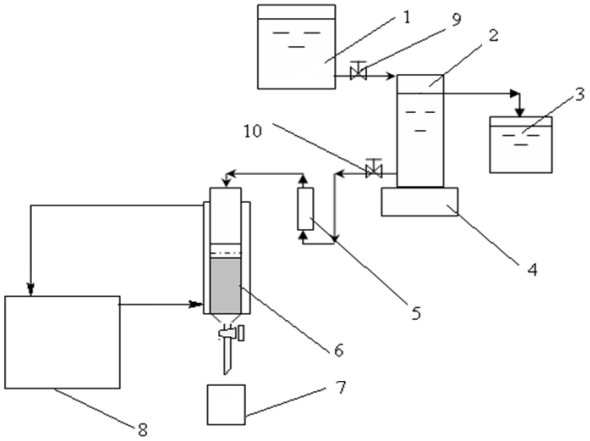

Figure 1. Experimental installation for the sorbtion study. dynamic regime

The content of iron for solutions was determined using a spectrophotometric method with 1.10 - phenantroline and hydroxilaminochlorohidrat (λ = 510nm) and Hach DR/2000 spectrophotometer (Düsseldorf. Germany) [6.7]. For plotting calibration curve was used $FeSO_4 \cdot 7H_2O$ reference certified material from Merck (Darmstadt. Germany). Because in the presence of dissolved O_2 a part of Fe(II) oxidizes to Fe(III). in all experiments was measured the concentration of total iron as Fe(II) ions. For reproductible results. the experiments were conducted in three replicates.
The studies have followed the influence of parameters like flow and the concentration of influent solution on exchange capacity in dynamic regime. PH was kept at constant value of 2.3 due the solubility causes and operating pH range for resin.

So. Fe(II) precipitates at pH = 4 - 12 depending on his concentration. Fe(III) derived from the oxidation of Fe(II) in the presence of oxygene precipitates at pH around 2.5 and operating range for Purolite resin is between 2 and 6.

In experiments flow was varied between 0.5 and 2 ml/minute. The range of Fe(II) concentration in influent solution was between 100 and 200 mg Fe(II)/L. Work temperature was 22^{o}C.

3. Results and discussions

3.1. The influence of feeding flow against exchange capacity. To find usable capacity exchange of Purolite S930 resin was made experiments using 34% $CaCl_2$ solutions with 200 mg/L iron content. resin dose 4g (10.2 ml) varying power flow of the column between 0.5 and 2 ml/minute. Experimental conditions are shown in Table 3. The breakthrough time of the column and usable capacity of the resin at breakthrough are shown in Table 4. The breakthrough time was determined as the time of operation of the column after its effluent concentration has a concentration in Fe (II) lower than 10 mg/L. according with STAS 2073-75. Calcium chloride.

From table 4 it can see the decreasing volume of treated solution and breakthrough time with the increasing of feeding flow. Plotting the dependence between the usable capacity breakthroughs and feeding flow (figure 2). it results the increasing of usable capacity breakthrough of Purolite S930 resin with the increasing of feeding flow. as expected. Time to exhaustion the resin is the time after which the concentration in Fe(II) of the eluate is equal to the concentration in the initial solution. table 5.

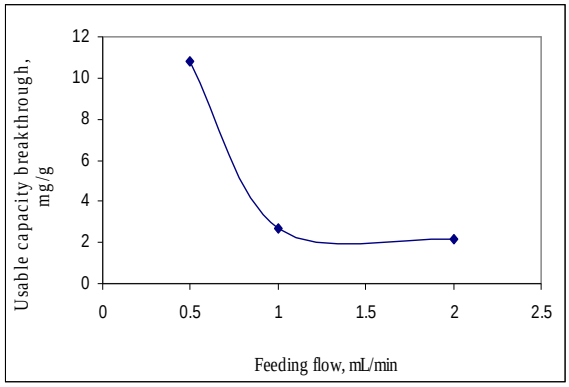

Figure 2. Variation of usable breakthrough capacity with feeding flow.

Figures 3 and 4 show the variation of concentration in the column effluent depending on the volume passed through the column. and respectively the variation of concentration in the column effluent. depending on operation time.

Table 3.
Experimental conditions in the study of the influence of flow on exchange capacity

Nr.	**pH_i**	**T** (ºC)	**C_o** mg Fe(II)/L	**Resin volume** (mL)	**Layer heihgt** (cm)	**Time** (h)	**Feeding flow** (mL/min)
1	2.3	22	200	10.2	13	0 - 60	0.5
2							1.0
3							2.0

Table 4
Usable breakthrough capacity of Purolite S930 resin for sorbtion of Fe (II) from 34%CaCl2 solution

Nr.	**Feeding flow** (mL/min)	**Breakthrought time** (min)	**Purged solution volume** (mL)	**Usable capacity breakthrough** (mg/g)
1	0.5	469	220.85	10.8
2	1.0	57	54	2.6
3	2.0	25	44	2.1

Table 5.
Usable exhaustion capacity of Purolite S930 resin for sorbtion of Fe (II) from 34% CaCl2 solution

Nr.	Feeding flow (mL/min)	Solution volume passed through column (mL)	Exhaustion time (h)	Usable capacity exhaustion (mg/g)
2	1.0	1957	32	179

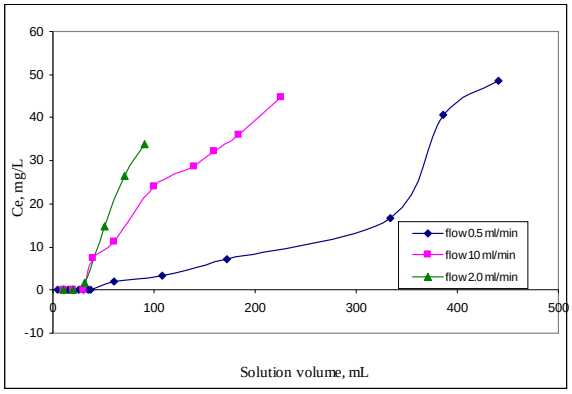

Figure 3. Variation of the effluent concentration depending of volume passed

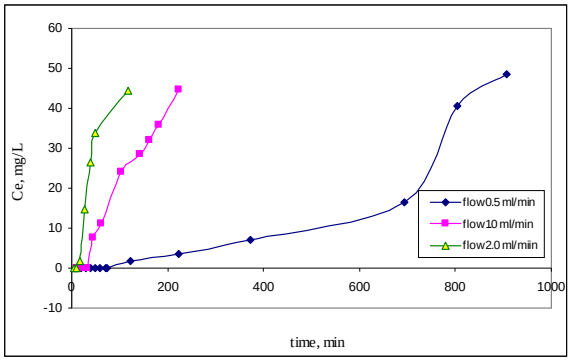

Figure 4. Variation of the effluent concentration depending of operating time.

3.2 Influence of initial concentration of the solution on the exchange capacity. To study the influence of initial concentration in sorbtion of Fe(II) ions on Purolite S930 resin in dynamic regime. the experiments was made on the same column using 4 g of resin (10.2 ml). power flow 2 ml/minute and variable concentration for Fe(II). like in table 6. Breakthrought times of the column and usable capacity to breakdown are presented in table 7 Table 7 shows the decrease of usable capacity to breakthrought with the increasing of the initial feeding concentration (C_o). Also for 4g resin dose and feeding flow of 2 ml/minute it observed the decreasing of refined solution volume and breakthrought times with the increasing of concentration of Fe(II) in feeding solution. Plotting the breakthrought usable capacity function of initial concentration of iron in initial feeding solution observe it's increasing with the decrease of Fe(II) concentration in feeding solution. Figure 5. Variation of column effluent concentration in time is plotted in Figure 6.

Table 6.
Experimental conditions in the study of the influence of initial concentration of Fe(II) in $CaCl_2$ solution. on usable capacity

Nr. exp.	pH_i	T (°C)	Feeding flow (mL/min)	Resin volume (mL)	Layer heihgt (cm)	Time (h)	C_o (mg Fe(II)/L)
1	2.3	22	2	10.2	13	25 - 30	100
2							150
3							200

Table 7.
Experimental conditions in the influence of initial concentration of Fe(II) in $CaCl_2$ solution. on usable capacity

Nr. exp.	C_o (mg Fe(II)/L)	Breakthrought time (min)	Volume of refined solution (mL)	Usable capacity breakthrough (mg/g)
1	100	208	387	197
2	150	28	55	2.7
3	200	25	44	2.16

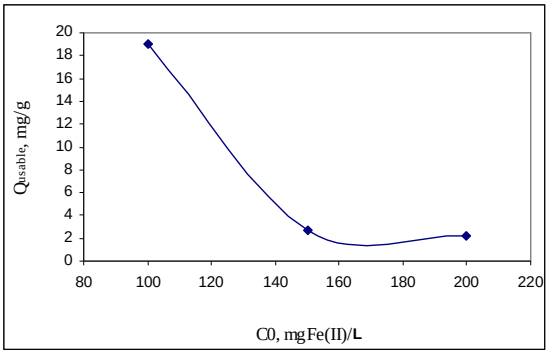

Figure 5. Variation of breakthrought usable capacity function the concentration of Fe(II)

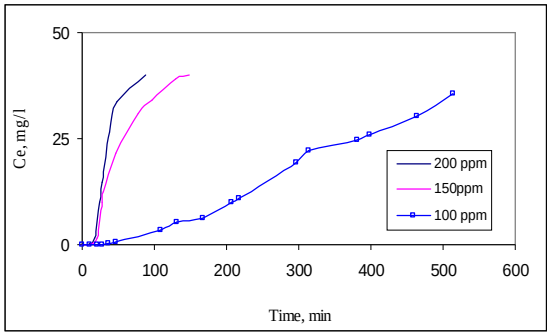

Figure 6. Variation of effluent concentration in time

3.3. Desorbtion efficiency. For the study of desorbtion efficiency the experiments were performed in the same column using HCl 2N and 10%. feeding flow rate 0.3 ml/minute. Figure 7 and 8 show the variation of eluent concentration as function of regeneration solution for 2g and 4 g of resin. As seen in table 8 and 9. increasing the resine dose and the concentration of the regeneration solution. the degree of concentration for iron have superior results**:** concentration degree increases from 50 to 520 times. maximum concentration from eluate increases from 9.86 g/L to 104 g/L. concentration peak from eluate also increases from 24.6 g/L to 172 g/l.

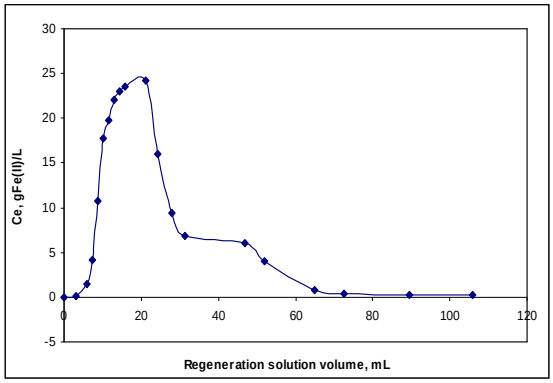

Figure 7. Variation of eluent concentration with solution regeneration volume. 2 g resin dose. flow 0.3ml/minute. HCl 2N.

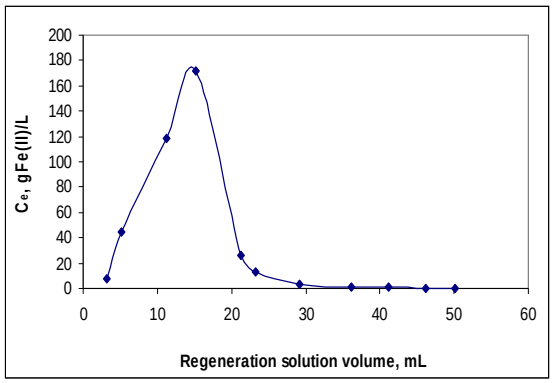

Figure 8. Variation of eluent concentration with solution regeneration volume. 4 g resin dose. flow 0.3ml/minute. HCl 10%.

Table 8.
Degree of Fe(II) concentration in eluate. resin dose 2g. HCl 2N

Resin dose (g)	Feeding flow. mL/min	Peak concentration of eluted iron. g Fe(II)/L	Maximum concentration of eluate. g Fe(II)/L	Degree of iron concentration
2	0.3	24.6	9.86	50

Table 9.
Degree of Fe(II) concentration in eluate. resin dose 2g. HCl 10%

Resin dose (g)	Feeding flow. mL/min	Peak concentration of eluted iron. g Fe(II)/L	Maximum concentration of eluate. g Fe(II)/L	Degree of iron concentration
4	0.3	172	104	520

4. Conclusions

Dynamic column experiments show that the resin is able to selectively remove iron from 34% calcium chloride solutions.

The resuls show that under circumstances ($T=22^0C$. volume of resin = 10.2 ml. layer heihgt=13 cm. pH=2.3) usable breakthrough capacity decrease with the increasing of feeding flow and increasing of the concentration of Fe(II) in feeding solution. The volume of refined solution decrease with the increasing of Fe(II) in feeding solution.

Usable capacity for sorbtion in dynamic regime is 197 mg Fe(II)/g. according to data from technical literature [4] and close with the value determined in batch process [3]. Efficiency of desorbtion increases with height of resin bad (dose) and HCl concentration.

5. References

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