STUDIA UBB CHEMIA, LVI, 1, 2011

EQUILIBRIUM AND KINETIC STUDIES OF IRON (II) REMOVAL FROM 34% CALCIUM CHLORIDE SOLUTIONS BY CHELATING RESIN PUROLITE S930

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ABSTRACT. This work presents equilibrium, thermodynamic and kinetic studies of iron removal from 34% $CaCl_2$ solution (that was obtained from electrolysis sludges) using chelating resin Purolite S930 with iminodiacetic acid functional groups.

Batch sorption experiments were performed using both forms of the resin (S930-Na and S930-H) by varying the initial conditions such as initial solution pH (2.0-5.0), initial concentration of iron (20-400mg/L), solution temperature (22-40^{0}C) and contact time (10 minutes up to 24 hours). The practical capacity of the resin increases with initial solution pH, temperature and the initial concentration of iron(II). Freundlich constants (n) had values bigger than 1 for the whole range of temperature that was studied, so, the sorbtion of iron on Purolite S930-Na form resin is a favourable one. The values of correlation coefficients (R^2) higher than 0,99 show that on the studied concentration (200-400mg Fe(II)/L) and temperature (295-313 K) range the data were more suitable to the LangmuirI model. The values obtained for the Langmuir (R_L) constant ($0 < R_L < 1$) show a favourable isotherme for the whole range of temperature that was studied (295-313 K). The maximum sorption capacity (q_{max}) was 238 mg Fe(II)/g for pH5. The values of calculated thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) indicate that the sorption of iron onto Purolite S930 resin is an endothermic and spontaneous process. The kinetic data show that, initially, sorption increases rapidly, but after that, the rate becomes slower; the equilibrium can be considered attained after 24 hours. Kinetic studies reveal that the sorption of iron from 34% $CaCl_2$ solution onto chelating resin follows a pseudo-second order model.

Keywords: *Iron (II) removal, Purolite S 930, Sorption isotherm, Thermodynamics, Kinetics*

INTRODUCTION

From chemical industry results important quantities of sludges. The most part of these sludges contain useful compounds that can be reused to obtain other chemical products. Depending on the method used to recover this compounds, the new chemical products may contain also heavy metals.

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The presence of the heavy metals in the environment is a major problem, so to find another purification technique than chemical precipitation is very important in environmental protection.

Ion exhange methodes are profitable and ecological as purification methodes and may be used for organic and inorganic compounds. Some advantages of these methodes are: good percent of removal, safe operation, easy to use, no sludges and recovery of the sorbed. Ion exhangers have also great exchange capacity, long operating life and big number of operating cycles[1, 2].

The aim of this work is to extend the application of Purolite S930 chelating resin for the purification of 34% $CaCl_2$ solution obtained from electrolysis sludges [3].

The sorption characteristics of iron ions onto iminodiacetic resin Purolite S930 was studied in various operating conditions like: initial pH, initial iron concentration, contact time, temperature, ionic form of the resin and resin dose.

RESULTS AND DISCUSSIONS

Sorption isotherms. The relationship between the amount of Fe(II) sorbed onto Purolite S930 and equilibrium concentration in 34% $CaCl_2$ solution is described by the sorption isotherms. The analysis of equilibrium data was used to verify the sorption models and also to determine the values of real sorption capacity.

The sorption of Fe(II) by Purolite S930 resin was quantitatively evaluated by percent of Fe(II) removal *R* (%) and by amount of Fe(II) retained on resin, *q* (mg/g), according to Eqs.1 and 2:

$$R = \frac{C_0 - C_e}{C_0} 100 ; \tag{1}$$

$$q = \frac{(C_0 - C_e)V}{m} ; \tag{2}$$

where C_0 and C_e are the initial and the equilibrium concentration of Fe(II) in the solution (mg/L), *V* is the volume of solution (L) and *m* is the amount of the resin (g).

Figure 1 shows the sorption isotherms of iron (II) from 34% $CaCl_2$ solution onto sodium form of Purolite S930 resin, for different values of solution pH. The influence of the initial iron concentration on loading capacity of the resin is presented in Figure 2.

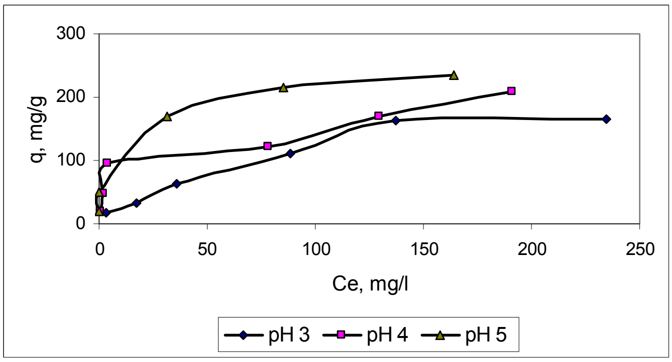

Figure 1. Isotherm plot for Fe (II) sorption onto Purolite S930-Na resin; T=22^{0}C, resin dose=1g/L, contact time=24h;

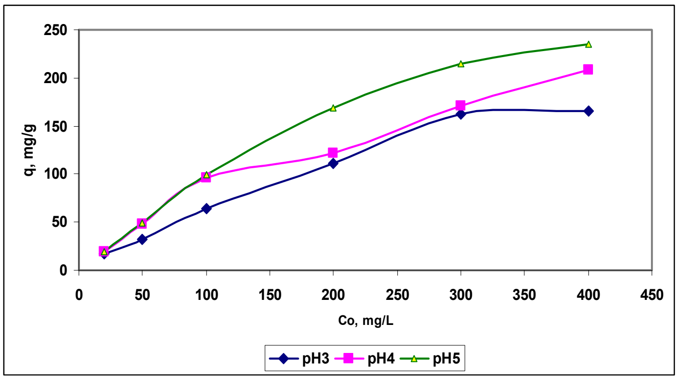

Figure 2. The influence of the initial iron concentration on loading capacity; T=22^{0}C, resin dose=1g/L, contact time=24h;

The equilibrium data obtained from sorption experiments were fitted using Freundlich, Langmuir and Dubinin models. The equation parameters of these models provide important information about the sorption mechanism, the surface properties and the affinity of the sorbent [6].

Freundlich model

The *Freundlich* equation is an empirical relationship established upon sorption onto a heterogeneous surface supposing that different site involve different sorption enegies.

$$q = K_F\, C^{1/n} \tag{3}$$

where K_F (mg/g) and n are Freundlich constants witch incorporate all factors affecting the sorption process such as sorption capacity and intensity of sorption. These constants are determined from the intercept and slope of linear plot of log q_e versus log C_e [7].

$$\lg q = \lg K_F + \frac{1}{n} \lg C_e \tag{4}$$

To determine the values of Freundlich parameters (K_F and *n*) the experimental data where plotted as *log q* versus *log C_e*, as shown in Figure 3.

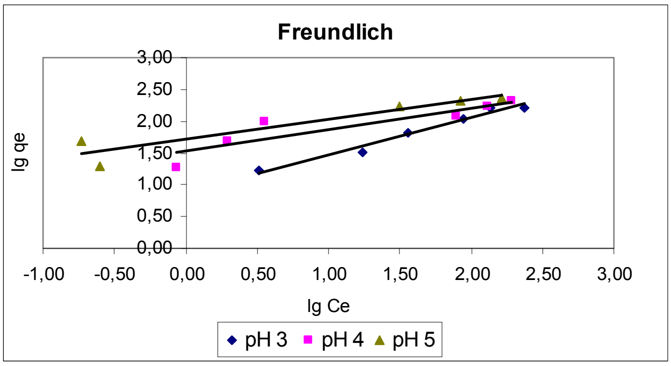

Figure 3. Freundlich isotherm plots for the sorption of iron (II) from 34%$CaCl_2$ solution onto Purolite S930-Na resin; T=22^{0}C, resin dose=1g/L, contact time=24h

Langmuir model

Langmuir sorption isotherm shows the maximum sorption capacity supposing monolayer sorption on a surface with a finite number of identical sites.

$$\frac{C_e}{q} = \frac{1}{q_{\max}} C_e + \frac{1}{K_L q_{\max}} \tag{5a}$$

$$\frac{1}{q} = \left(\frac{1}{K_L q_{\max}} \right) \frac{1}{C_e} + \frac{1}{q_{\max}} \tag{5b}$$

where q_{max} and K_L are Langmuir isotherm constants. Thus, q_{max} show the maximum sorption capacity (mg/g) while K_L is the equilibrium constant relating adsorption capacity (L/mg). Langmuir constants are evaluated from the slope and intercept of the C_e/q_e versus C_e. The dimensionless parameter of the equilibrium R_L was calculated using eq. 6.

$$R_L = \frac{1}{1 + K_L \cdot C_0} \tag{6}$$

where C_0 (mg/L) is the initial metal ion concentration. This parameter may have four values: R_L = 0 for an irreversible sorption isotherm, 0 < R_L < 1 for a favourable sorption isotherm, R_L = 1 for a sorption linear isotherm and R_L >1 for an unfavourable sorption [7].

The equilibrium data were also fitted to linear Langmuir I and Langmuir II equations (5a, 5b). The Langmuir parameters (q_{max} and K_L) were determined by plotting Ce/q_e versus C_e (Fig. 3.4.) and $1/q_e$ versus $1/C_e$ respectively (Figure 4 and Figure 5).

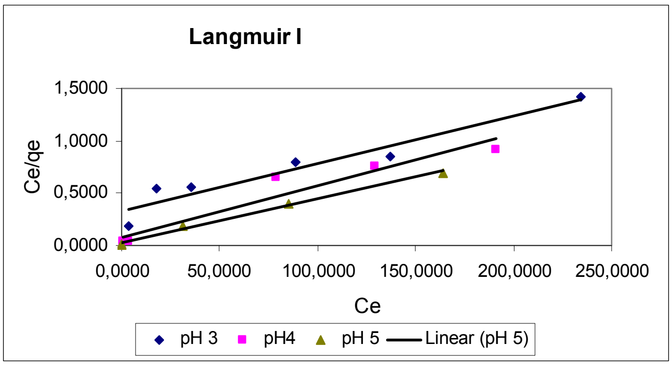

Figure 4. Langmuir I isotherm plots for the sorption of iron(II) from 34%$CaCl_2$ solution onto Purolite S930-Na resin; T=22^{0}C, resin dose=1g/L, contact time=24h;

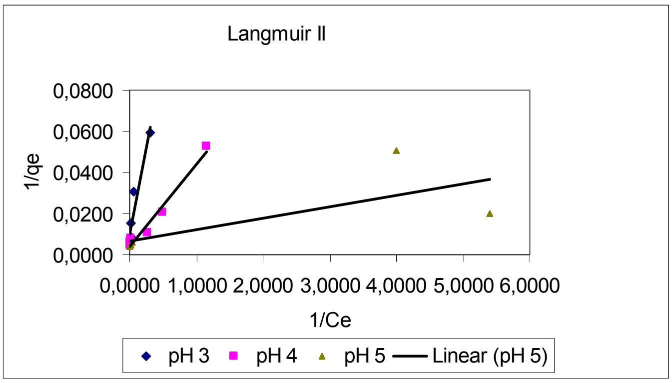

Figure 5. Langmuir II isotherm plots for the sorption of iron(II) from 34%$CaCl_2$ solution onto Purolite S930-Na resin; T=22^{0}C, resin dose=1g/L, contact time=24h;

For defining the model wich describes in the best way possible the experimental data, there were used linear regression analysis.

The values of isotherm parameters for different initial pH are presented in Table 1.

The high coefficient of determination (R^2 = 0.994) of the plot shows that the linear Langmuir equation gives the best fit to the sorption isotherm for the sorption of Fe(II) onto Purolite S930 resin at 295 K. For an initial pH = 5 and a temperature of 295 K, the Langmuir maximum sorption capacity q_{max} was 238 mg Fe (II)/L and the Langmuir equilibrium constant K_L, had a value of 0.178 L/g.

Table 1. pH dependence of the isotherm parameters for iron(II) sorption onto Purolite S930 resin from 34% $CaCl_2$ solutions at T = 295 K

	pH=3	**pH=4**	**pH=5**
Freundlich	y=0.583x+0.887 R^2=0.974 n=1.71 K_F =7.72	y=0.342x+1.526 R^2=0.823 n=2.92 K_F =33.59	y=0.202x+0.888 R^2=0.567 n=4.92 K_F =77.57
Langmuir I	y=0.004x+0.336 **R^2=0.928** q_{max} =222.2mg/g K_L=0.107L/mg = 6000 L/mol ΔG= - 21337.27 kJ/mol	y=0.005x+0.072 **R^2=0.937** q_{max} =200 mg/g K_L=0.069 L/mg = 3872.75 L/mol ΔG= - 20263.5 kJ/mol	y=0.004x+0.023 **R^2=0.994** q_{max} =238.1 mg/g K_L=0.178 L/mg = 9974.04L/mol ΔG= - 22441.56 kJ/mol
Langmuir II	y=0.168x+0.0095 R^2=0.915	y=0.039x+0.0041 R^2=0.966	y=0.005x+0.0068 R^2=0.518
Dubinin	y=-0.0053x+7,30 β=0.006mo l^2/J^2 q_{max}=793.14 mg/g R^2=0.936 *E*=9.12 kJ/mol	y=-0.0027x+6,25 β=0.004mo l^2/J^2 q_{max}=384.9 mg/g R^2=0.992 *E*=11.18 kJ/mol	y=-0.0041x+5,95 β=0.002mo l^2/J^2 q_{max}=519.57 mg/g R^2=0.797 *E*=15.81kJ/mol

Each ,,*R^2*” value, was calculated for 6 points of concentration: 20, 50, 100, 200, 300, 400 mg Fe(II)/L.

Figure 6 shows the variation of sorption intensity (R_L) with initial metal concentration in the 34% $CaCl_2$ solution, for the range of pH (3-5) and temperature 295 K.

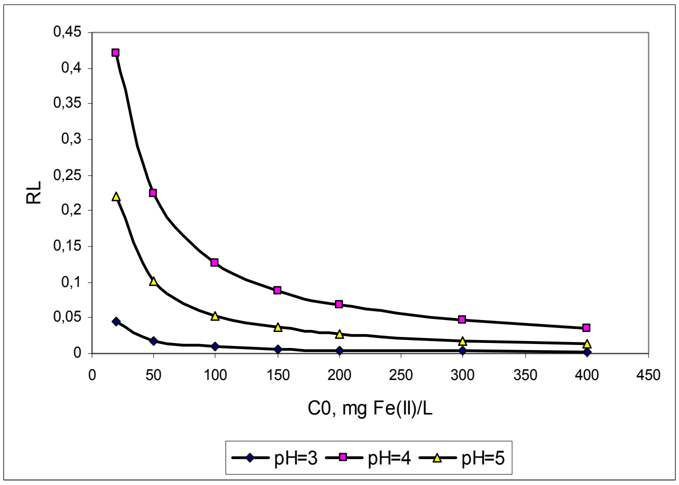

Figure 6. Variation of sorption intensity (R_L) with initial metal concentration; 34%$CaCl_2$ solution, 1 g/L S930 - Na, contact time 24 h, pH = 3-5, temperature: 295 K

The values for sorption capacity q_{max}=200-238 mg/g are comparable with literature data that are described in Table 2 [4].

The Dubinin–Radushkevich isotherm is expressed in linear form as follows [8,9].

$$\ln q = \ln q_{\max} - \beta \varepsilon^2 \tag{7}$$

where q_{max} is the maximum sorption capacity (mg/g), β, the activity coefficient related to mean sorption energy (mol^2/J^2) and ε is the Polanyi potential (J/mol) equal to:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{8}$$

where R is the gas constant and T is the temperature. The mean free energy of sorption, E (kJ/mol), can be estimated using the following equation:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{9}$$

Table 2. Sorption capacity for Fe(III) on different kinds of resins

Metal	Resin	Loading capacity, mg/g
Fe(III)	Amberlite IRC-50	200
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

The mean free energy of sorption *E*, gives information about the type of the sorption mechanism as chemical, ion-exchange or physical sorption.

If ,,*E”* value is between 8 and 16 kJ/mol, the sorption process follows a chemical ion-exchange; if ,,E” value is less than 8 kJ/mol, the sorption is physical [7].

To determine the nature of sorption process (physical or chemical), the experimental data were fitted to the *Dubinin isotherm model* based on the heterogeneous surface of the sorbate (Figure 7).

The isotherm parameters were computed from the graphical representation of $\ln q = f(\varepsilon^2)$ equation. (Table 1). The value of the mean free energy of sorption *E* calculated with Eq. (9) was 11.62 KJ/mol indicating that the sorption process follow a chemical ion-exchange mechanism.

The validity of Freundlich and Langmuir models within the range of 295-313 K. The isotherms for this range of temperature are presented in Figure 8 and the results are shown in Table 3.

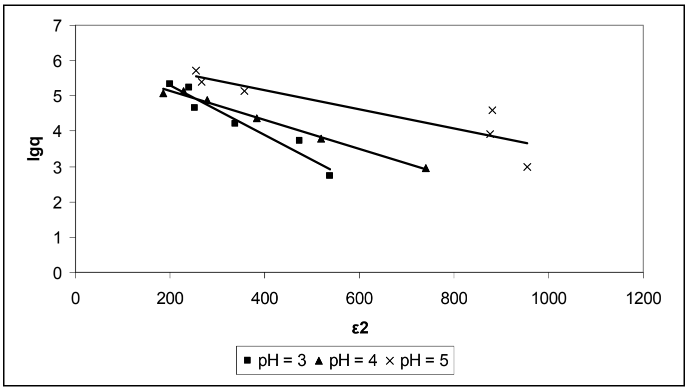

Figure 7: D-R isotherm plots for the sorption of Fe (II) from $CaCl_2$ 34% solution, onto S930 – Na resin;1 g/L S930-Na, contact time 24 h, temperature: 22 ºC

The high coefficient of determination (R^2) of the plot shows that the linear Langmuir equation gives the best fit to the sorption isotherm for the sorption of Fe(II) onto Purolite S930 resin in the whole range of temperature that was studied.

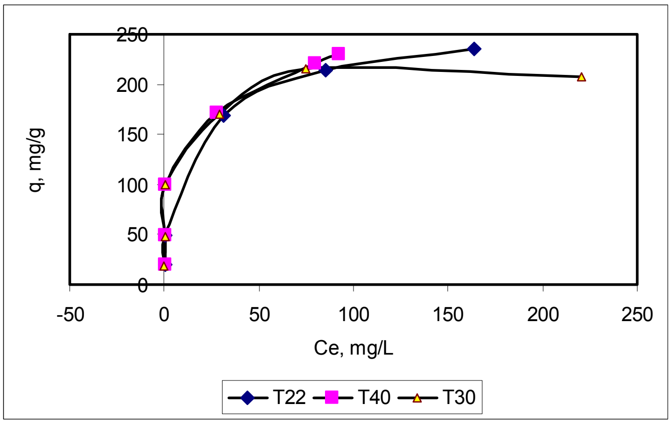

Figure 8. Sorption isotherms from iron(II) onto Purolite S930-Na form resin, different temperatures, 34% $CaCl_2$ solution

Table 3. Temperature dependence of the isotherm parameters for iron(II) sorption onto Purolite S930-Na form resin from 34% $CaCl_2$ solutions at pH=5

	T=295K	**T=303K**	**T=313K**
Freundlich	y=0.202x+0.888 R^2=0.56 n=4.92 K_F =77.5711	y=0.271x+1.802 R^2=0.82 n=3.68 K_F =63.44	y=0.309+1.820 R^2=0.78 n=3.24 K_F =66.17

	T=295K	T=303K	T=313K
Langmuir I	y=0.004x+0.023 **R^2=0.994** q_{max} =238.1mg/g K_L=0.178 L/mg = 9974.04L/mol ΔG = - 22441.5 J/mol	y=0.004x+0.005 **R^2=0.939** q_{max} =267.8 mg/g K_L=0.183 L/mg = 10265.62L/mol ΔG = - 23279.7 J/mol	y=0.003x+0.016 **R^2=0.937** q_{max} =272.3 mg/g K_L=0.206 L/mg = 11540.46L/mol ΔG = - 24352.4 J/mol
Langmuir II	y=0.005x+0.006 R^2=0.519	y=0.004x+0.004 R^2=0.990	y=0.007x+0.002 R^2=0,77

The values for sorption intensity ($0 < RL < 1$) describes a favourable isotherm for the whole range of temperature (295-313 K), Figure 9.

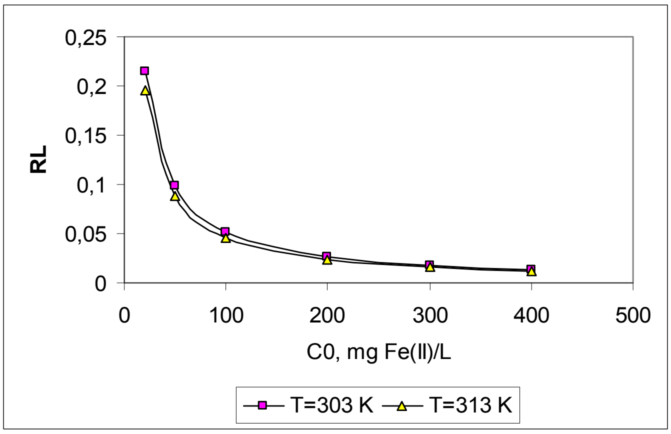

Figure 9. The variation of sorption intensity (R_L) with initial metal concentration for different temperatures; 1 g/L S930 – Na form, contact time 24 h, pH = 5.

Thermodynamic studies

The thermodynamic parameters for sorption of iron (II) on Purolite S930 chelating resin were evaluated using the Langmuir equilibrium constant, K_L, which depends on temperature. The free energy (ΔG^o), was evaluated using equation [10].

$$\Delta G^{O} = -RT\ln K_L \tag{10}$$

where R is the gas constant (j/mol*K) and T is the temperature (^{0}K). The standard enthalpy (ΔH^o) and standard entropy (ΔS^o) associated to the sorption process were calculated by Eq**.** (8) [7].

$$\ln K_L = \frac{\Delta S^{O}}{R} - \frac{\Delta H^{O}}{RT} \tag{11}$$

The Gibbs free energy change of sorption (ΔGº) values calculated using Eq.(7) for different temperatures are presented in Table 4.

Table 4. Thermodynamic parameters for iron(II) sorption onto Purolite S930-Na form resin

T, K	ΔG^0, kJ/mol	ΔH^0, kJ/mol	ΔS^0, J/mol.K
295.15	-22.59	6.31	97.84
303.15	-23.28		
313.15	-24.35		

The negative value of free energy *ΔGº* indicated us that sorption of Fe (II) onto Purolite S930-Na form resin is spontaneous from thermodynamical point of view. In addition, the decrease in *ΔGº* values with increase in temperature shows that the sorption was favourable at higher temperatures. The enthalpy change (ΔHº) and the entropy change(*ΔSº*) for the sorption process were obtained from the *ln K* versus *1/T* plot (Figure 10). The enthalpy change (ΔHº) was 6.31 kJ/mol. The positive value indicates the endothermic nature of the sorption process. The positive value of the entropy change (ΔSº=97.84 j/mol K) proves the affinity for iron(II) sorption onto Purolite S930 chelatic resin.

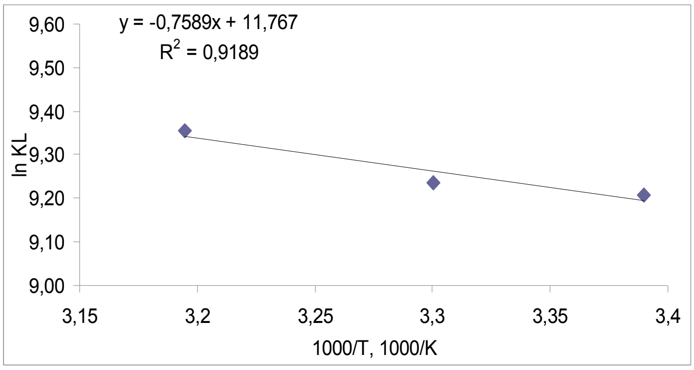

Figure 10. Dependence of *ln* K_L vs. *1/T* for Fe(II) sorption onto Purolite S930-Na

Sorption kinetics

The effect of the phases contact time on Fe (II) sorption onto sodium ionic form of the resin Purolite S930 is presented in Figure 11. The experiments were conducted using solutions of 200 mg Fe (II) /L at temperature 295 K and the initial pH = 5.

The equilibrium was considered attained after 24 hours; a further increase in contact time has a negligible effect on the percent of removal.

The sorption of Fe (II) onto Purolite S930-Na form resin was investigated in terms of the kinetics of the sorption mechanism by using two models: Lagergren and Ho.

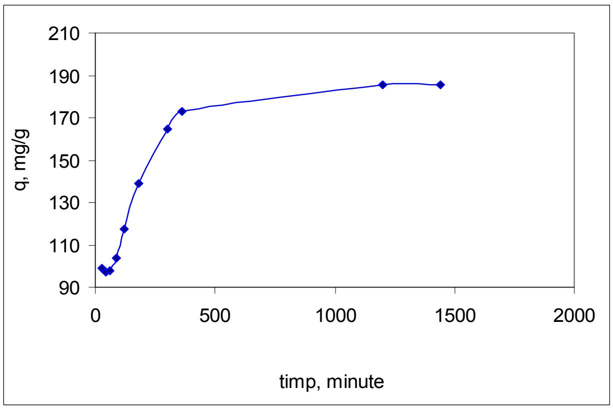

Figure 11. Effect of contact time on the Fe (II) removal on S930-Na form resin: C_0 = 200 mg Fe(II)/L, pH = 5, T = 295 K, resin dose = 1g/L

Pseudo-first-order model (Lagergren)

The pseudo-first-order rate expression is presented in Eq. (12)

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2{,}303}t \tag{12}$$

where, q_e is the amount of Fe (II) sorbed at equilibrium (mg/g), q is the amount of Fe (II) sorbed at time t (mg/g) and k_1 is the rate constant of first order sorption (min^{-1}).

The values of pseudo-first-order model parameters (k_1 and q_e) were determined by plotting $ln\ (q_e - q_t)$ versus t, and the values of pseudo-second-order model parameters (k_1 and q_e) were determined by plotting t/q_t versus t (Figure 12 and Figure 13). The values of parameters calculated for various initial concentrations and various temperatures are presented in Table 5.

Pseudo-second-order model (Ho)

The pseudo-second-order rate expression is presented in Eq. (13)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{1}{q_e}t \tag{13}$$

where k_2 (g/mg min) is the rate constant of the second-order equation; q_t (mg/g), the amount of sorption time t (min) and q_e is the amount of adsorption equilibrium (mg/g).

The initial sorption rate, *h* (mg/ g. min), at *t* = 0 is defined as:

$$h = k_2 q_e^2 \tag{14}$$

where q_e and *h* values were determined from the slope and intercept of the plots of *t/q* against *t*.

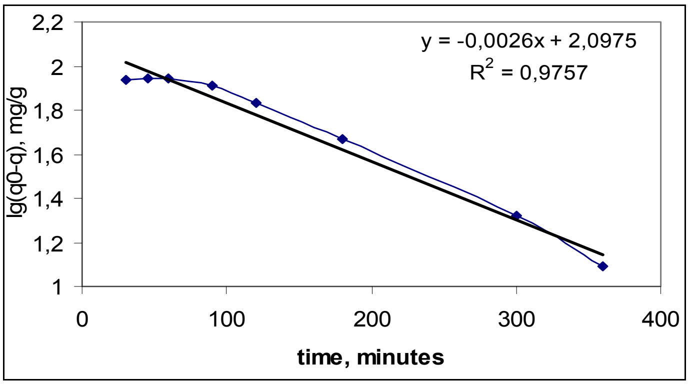

Figure 12. Lagergren-first-order model, Fe(II) sorption onto Purolite S930-Na form resin, C_0=200 mg Fe(II)/L, T=295 K

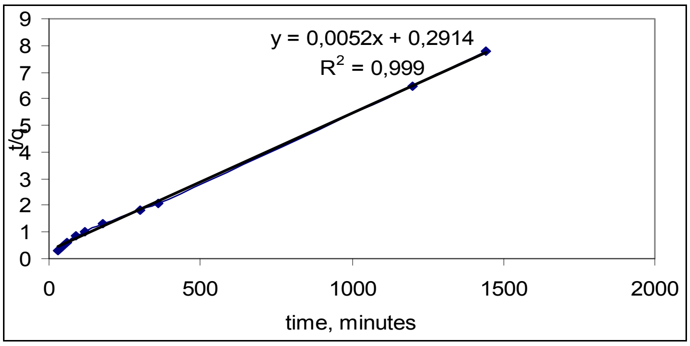

Figure 13. Ho pseudo-second-order model, Fe(II) sorbtion onto Purolite S930-Na resin, C_0=200 mg Fe(II)/L, T=295 K

Table 5. Pseudo first-order and pseudo-second-order parameters for the sorption of Cu (II) onto Purolite S930 at various temperatures and various initial concentrations

T (^{0}K)	Pseudo first-order model			Pseudo second-order model			
	k_1, min^{-1}	$q_{max,}$ mg/g	R^2	k_2, g/mg min	$q_{max,}$ mg/g	h, mg/ g. min	R^2
C_0 = 200 mg Fe(II)/L							
295	$5.98 \cdot 10^{-3}$	125.7	0.9757	$7.87 \cdot 10^{-6}$	192.3	3.43	**0.9999**

The results presented Table 5 reveal that the pseudo-second-order kinetics is expected to be followed in the sorption of Fe(II) onto Purolite S930 resin since the values of R^2 (0.9999*)* are higher than values obtained for pseudo first-order. Also, the value for sorption capacity (q_{max}) for this model is close to experimental sorption capacity values.

EXPERIMENTAL

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 6. The resin was dried in an oven at 65 ºC.

Table 6. Proprietes of chelating resin *

Polymer matrix structure	Macro porous 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 stock solution of iron (2000 mg Fe (II)/L) was prepared from analytical-reagent grade iron sulphate ($FeSO_4.7H_2O$) in distilled water and hydrochloric acid, analytical-reagent grade.

The work solutions were prepared from stock solution using different aliquot parts for the range of concentration 20-400 mg Fe (II)/L, respective: 1mL; 2.5mL; 5mL; 15mL; 20mL; 25 mL of stock solution. Required pH adjustments of the solutions were performed with hydrochloric acid or calcium hydroxide solution.

The calcium chloride 34 % solution was prepared using calcium chloride pro analysi and distilled water.

Sorption experiments. Sorption of Fe(II) ions on Purolite S930 in sodium (S930-Na) and hydrogen (S930-H) forms was carried out in batch experiments using amounts of 100 mL of $CaCl_2$ 34% solution with different initial concentrations in Fe(II) (20–400 mg Fe (II)/L) that where added to Erlenmeyer flasks already containing the required quantity of 0.1g dried resin. The initial pH of the solutions was adjusted using diluted solutions of HCl or $Ca(OH)_2$ solution. The flasks where mechanically shacked at several fixed temperatures and at the rate of 120 cycles min^{-1} using Orbital Shaking Incubator GFL3031. After equilibrium (24 hours), the resin and solution were separated by filtration. The iron content of the solution and also the final pH of solution (pH_e) were measured.

For kinetic experiments the samples were analyzed after a specified period of time. For thermodynamic studies the experiments were repeated in the same conditions but for different temperatures. The concentration of Fe(II) in solutions was measured using a spectrophotometric method with 1,10-phenantroline and hydroxilaminochlorohidrat (λ=510nm) using Hach DR/2000 spectrophotometer [5]. Because in the presence of O_2 from air a part of Fe(II) becomes Fe(III),all experiments measured the concentration of total iron as Fe(II).

CONCLUSIONS

The *equilibrium data* were analysed using Freundlich, Langmuir and Dubinin sorption isotherm models; sorption was best fitted by the Langmuir 1 model. The values of sorption intensity ($0 < RL < 1$) indicate that iron(II) sorption onto Purolite S930-Na form resin has a favourable sorption isotherm and the resin is a good sorbent for the sorption of iron(II) from 34% $CaCl_2$ solution.

Thermodynamic studies reveal the big affinity of the sorbent for Fe(II) ions from 34% $CaCl_2$ solution and the endothermic nature of sorption process. The negative value of free energy ΔG^o indicated us that sorption of Fe (II) onto Purolite S930-Na form resin is spontaneous from thermodynamical point of view. The positive value of enthalpy change (ΔH^o = 6.31 kJ/mol) indicates the endothermic nature of the sorption process. The process is favourable at higher temperatures; the growth of temperature is favourable for the velocity constant (k). The positive values for ΔS^0 reveal the increasing disorder of the system.

The *kinetic studies* show that the sorption process of Fe(II) from 34% $CaCl_2$ solution onto Purolite S930-Na form resin follows a pseudo-second-order model.

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