

IRON REMOVAL FROM WASTEWATER USING CHELATING RESIN PUROLITE S930

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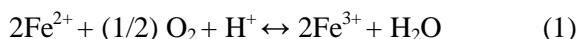
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Abstract: The work presents the sorption characteristics of Iron (II) on iminodiacetic resin Purolite S930 in various operating conditions such as initial pH, copper concentration, contact time, temperature, ionic form of the resin and resin dose. The percent of Iron (II) removal has a maximum at pH 5.0, and increases with the increasing of resin dose, of the contact time and decreases with increasing initial concentration of solution.

Keywords: iron, sorption, chelating resin, wastewater

1. Introduction

In water (drinking water, water supplies and wastewater) the Iron causes problems, such as giving reddish color and odor [3]. In general in water, iron exists in soluble form as Iron (II) and is oxidized to ferric iron according to eq. 1 [3].



The state of iron in water depends on the hydrogen concentration and the redox potential. With the increasing of the hydrogen concentration, dissolved iron (Fe^{2+} or Fe^{3+}) hydrolyzes to form precipitates. The ferrous ion hydrolyzes to produce the array of mononuclear species FeOH^+ to $\text{Fe}(\text{OH})_4^{-2}$ between pH 7 and 14 [10].

There are several methods for removal of iron and other heavy metals, used in water purification processes (drinking water treatment and wastewater treatment. All techniques have their advantages and limitations in application [4].

The most important techniques are chemical precipitation, coagulation–flocculation, flotation [6], [4], membrane filtration: ultrafiltration, nanofiltration [1] and reverse osmosis; electrochemical treatment techniques: electro dialysis, membrane electrolysis and electrochemical precipitation, electroextraction [9];

sorption treatment techniques: ion exchange [7]., adsorption [12], biosorption [11].

As other heavy metals the presence of iron in the environment is a major concern due to their non-biodegradability, bioaccumulation tendency, persistence in nature and toxicity to many life forms. Therefore, treatment of wastewaters containing heavy metal ions before discharge is an important component of water pollution control and becomes more important with the increasing of industrial activities

Iron (II) ions have a high solubility in the aquatic environment and can be absorbed by plants and living organisms. The maximum acceptable concentration of Iron (II) in drinking water recommended by World Health Organization (WHO) is 0.2 mg/L. The limit of Iron (II) into wastewater 5 mg/L according to Romanian regulation (NTPA001/2005).

Compared with other usual methods, ion exchange provides some advantages and is one of the most widely used techniques for treatment of wastewaters in many chemical process industries (Macoveanu et al., 2002). The efficient removal of metals ions requires an exchange material which can function in severe environments, exhibit a high affinity for the metal of interest and can be readily

regenerated. Due to their physical and chemical properties chelating resin are generally efficient in the removal of heavy metals ions from waste effluents.

2. Experimental

2.1. Materials

In the experiments was used the S930 chelating resin obtained from Purolite International Limited (Hounslow, UK). The main physical and chemical properties of the resin are presented in Table 1.

The stock solution of iron (II) (500 mg/L) was prepared from analytical-reagent grade copper sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in distilled water. Required pH adjustments were performed with sulphuric acid.

2.2. Sorption experiments

To avoid the iron precipitation in alkaline solution the hydrogen resin form was converted into sodium resin form. For the conversion of the resin was used 10% HCl solution. The process was followed by washing with distilled water until the pH of the effluent dropped to neutrality. The hydrogen resin form has been dried at 60 °C using an oven.

Sorption of iron (II) ions on Purolite S930 in hydrogen (S930-H) form was carried out in batch experiments using 50.0 mL of iron (II) solutions with different initial concentrations (10–300 mg/L) that were added to Erlenmeyer flask already containing 0.05 g of dry resin. The initial pH of the solution was adjusted by using diluted solutions of H_2SO_4 or 10 mL of acetate buffer solutions and

measured with WTW pH/cond 340i. The flasks were mechanically shaken at several fixed temperatures and at the rate of 120 cycles min^{-1} using Orbital Shaking Incubator GFL 3031. After equilibrium (24 hours), the resin and solution were separated by filtration and the iron content of the solution and, also, the final pH of solution (pH_e) were measured. In the experiments concerning the effect of the resin dose, a range of resin samples from 0.01 to 0.2 g was used. For contact time experiments, the procedures were the same as those presented in equilibrium experiments but the samples were analyzed after a specified period of contact time.

The concentration of Fe(II) in solutions was measured using a spectrophotometric method with 1,10-phenantroline and hydroxylaminochlorohidrat ($\lambda=510\text{nm}$) using Hach DR/2000 spectrophotometer [8]. 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) [7].

The sorption of Iron (II) by Purolite S930-H resin was quantitatively evaluated by percent of Iron (II) removal R (%) and by amount of Iron (II) retained on resin, q (mg/g):

$$R = \frac{C_0 - C_e}{C_0} 100 \quad (2)$$

$$q = \frac{(C_0 - C_e)V}{m} \quad (3)$$

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

Table 1. Characteristic properties of the chelating resin used*

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	70°C
Particle size range	+ 1.0mm <10%, -0.3mm <1%
Total exchange capacity	$\geq 1,9$ meq/mL

* Manufacturer supplied.

3. Results and discussion

3.1. Effect of solution pH

Sorption of Iron ions on chelating resins Purolite S930 involve an ion exchange process in conjunction with the formation of a coordinate bond. The ability to bind metal ions through amine groups lead to the grater selectivity for heavy metals from wastewaters. The formation and stability of the chelates with many metal ions are very dependent on the solution pH. Because the functional iminodiacetate groups of the Purolite S930 are weak acids, they are very selective for hydrogen ions (their dissociation is dependent on pH) [2].

In order to investigate the influence of initial solution pH on the Iron (II) removal by S930 resin, experiments were carried out using a resin dose (S930-H) of 1g/L and the initial iron concentration of 300 mg/L at 293.15 K. The initial solution pH was adjusted using H₂SO₄ diluted solutions. The correlation between the initial pH of solution and Iron (II) equilibrium concentration and the percent of Iron (II) removal, respectively, is illustrated in Figure 1.

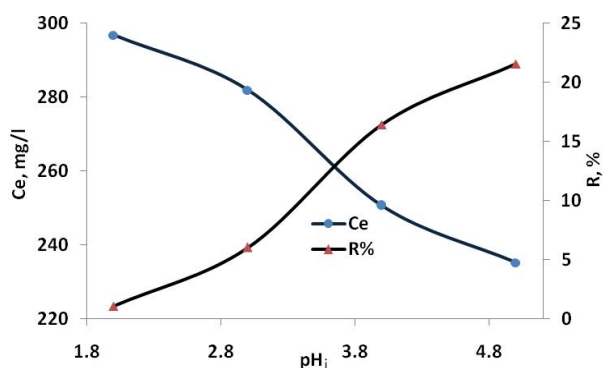


Figure 1: Effect of solution acidity on Iron removal onto S930 resin in H⁺ form:

C₀ = 300 mg/L, T = 293.15 K, time = 24 h, resin dose = 1g/L

The results reveal that in strong acidic media (pH=2) most carboxylic functional groups are protonated but with increase of pH up to 4-5 they start to dissociate and can react with Iron ions. The equilibrium Iron concentration decreases from the initial value of 300 mg/L to 296.82 mg/L and 235.27 mg/L for initial pH 2 and pH 5, respectively.

Figure 2 illustrate the variation of sorption capacity of S930-H resin for Iron (II) ions as a function of the initial pH of solutions.

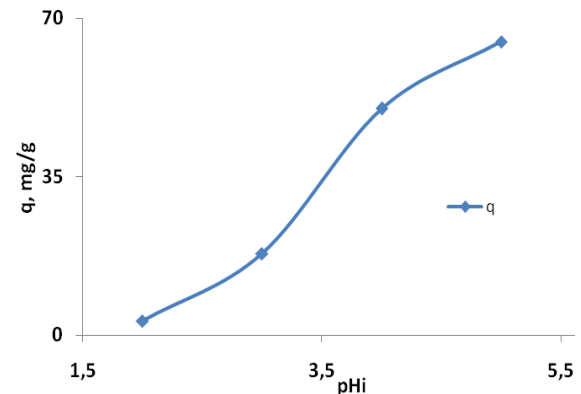


Figure 2: Effect of solution acidity on loading capacity of Purolite S930 resin in H⁺ form:

C₀ = 300 mg/L, T = 293.15 K, time = 24 h, resin dose = 1g/L

The loading capacity decrease significantly from 64 mg Iron (II) per gram resin for pH = 5 to 3.14 mg per gram resin for pH = 2. Figure 3 present a correlation between initial pH of the solution and equilibrium pH.

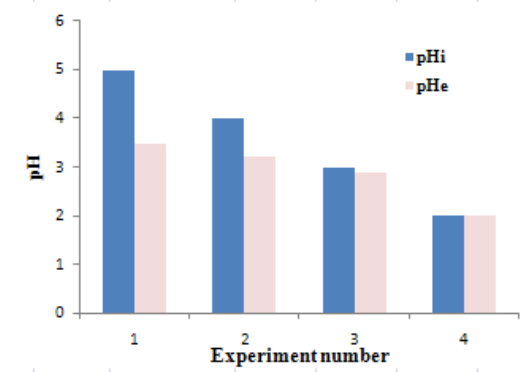
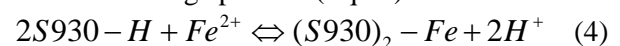


Figure 3: Comparison between initial hydrogen ions concentration (pHi) and equilibrium hydrogen ions concentration (pHe):

C₀ = 300 mg/L, T = 293.15 K, time = 24 h, resin dose = 1g/L, S930 resin in H⁺ form

Figure 3 shows that equilibrium pH are lower than initial pH and the difference from the initial pH and equilibrium pH decrease with decreasing of initial pH. The decrease of equilibrium pH can be explained by hydrogen ions releases in solution from ion exchange process (Eq. 4).



3.2. Effect of metal ion concentration

Metal ions sorption onto resin is strongly influenced by the initial metal ion concentration. The sorption data for Iron (II) ions on S930 resin in hydrogen form, namely removal percent and equilibrium concentration, as a function of initial

concentration of iron are showed in Figure 4 and figure 5, respectively. Experiments were carried out in solutions of pH=5 adjusted with sulphuric acid, at a resin dose of 1g/L and temperature 293.15 K.

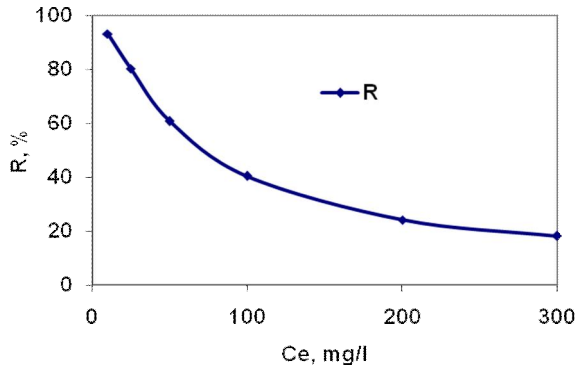


Figure 4: Effect of metal ion concentration on the Iron (II) removal percent onto S930-H: pH=5, time = 24 h, T = 293.15 K, resin dose = 1g/L

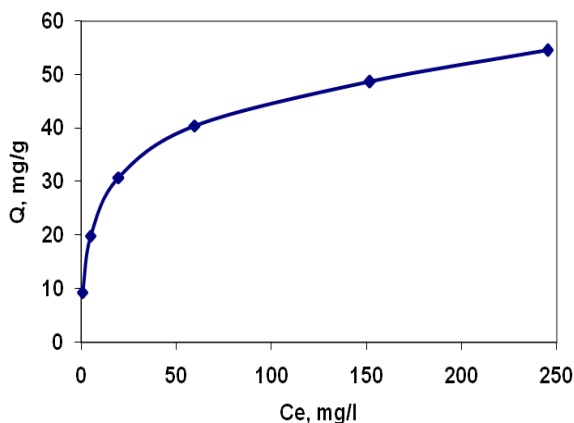


Figure 5: Effect of metal ion concentration on the Purolite S930-H loading capacity for Iron (II): pH=5, time = 24 h, T = 293.15 K, resin dose = 1g/L

Figure 4 reveals that with the increasing of Iron (II) concentration the percent of removal decrease but even for an initial concentration up to 25 mg Iron (II)/L, the percent removal was of 80%. Figure 5 shows that the Purolite S930-H loading capacity decreases with increasing of initial ion concentration.

3.3. Effect of contact time

The effect of the phases contact time on Iron (II) sorption onto hydrogen ionic form of the resin Purolite S930 is illustrated in Figure 6. The experiments were conducted using solutions of 100 mg Iron /L at temperature 293,15K; the initial pH = 5 was adjusted using H₂SO₄ diluted solutions.

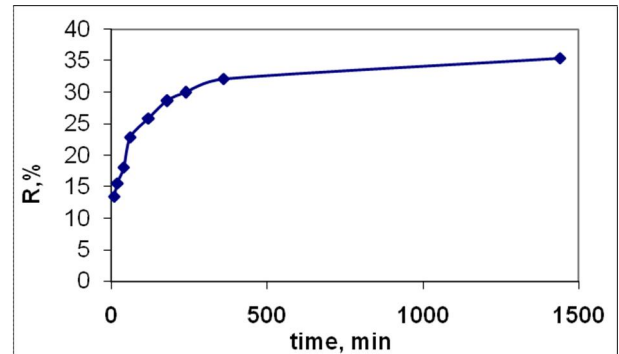


Fig.6. Effect of contact time on the Iron (II) removal on S930-H resin:

C₀ = 100 mg /L, pH = 5, T = 273.15 K, resin dose = 1g/L

The results reveal that within first 10 hours 40% sorption was occurred. The equilibrium was considered attained (reached) after 24 hours; a further increase in contact time has a negligible effect on the percent removal. The faster initial sorption rate may be explained by the greater number of resin sites available for the sorption of metal ions.

4. Conclusions

The present study shows that Purolite S930 is an effective sorbent for the removal of Iron (II) ions from aqueous solutions. The percent of Iron (II) removal has a maximum at pH 5.0 and increases with the increasing of resin dose, of the contact time and decreases with increasing of initial concentration of solution.

5 References

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