SELECTIVITY OF S 930 ION EXCHANGE RESIN REGARDING Ca^{2+} AND Ni^{2+} IONS FROM AQUEOUS SOLUTIONS

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Abstract

The natural water usually contents a series of the metallic ions, such as: Ca^{2+}, Mg^{2+}, K^+ and Na^+ that confer the test and quality of water, and also some heavy metals in trace like Ni^{2+}, Al^{3+}, Zn^{2+}, Cd^{2+}, Cu^{2+} etc that determine the toxicity of water. For obtaining potable water with quality according to European legislation is necessary to apply adequate methods to remove the heavy metals. Water pollution by toxic metals remains an important environmental issue having a major impact on the public health and the economy.

This paper present a comparative study of Ca^{2+} and Ni^{2+} ions sorption from aqueous solutions on S 930 ion exchange resin. The ion exchange capacity toward Ca^{2+} and Ni^{2+} ions depends on the pH values of the aqueous solution, increasing with the increase of pH value in the range of 2 – 6.5 pH unities. Simultaneous sorption on S 930 E of Ca^{2+} and Ni^{2+} ions from their binary mixed solutions was studied, the weight ratios between the two metals in the binary systems being 1:2, 1:1; 2:1 and 5:1, by the means of batch experiments performed at 20.0 ± 0.1^{o} C, at different pH values. Among the studied systems, Ni seems to have the strongest affinity for S930 ion exchange resin.

Keywords: S930 ion exchange resin, calcium, nichel, water treatment, removal

I. INTRODUCTION

Water pollution by toxic metals remains an important environmental issue having a major impact on the public health and the economy.The natural water usually contents a series of the metallic ions, such as: Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} that confer the test and quality of water and also some heavy metals in trace like Pb^{2+}, $Fe^{+2,}$ Fe^{+3}, Zn^{2+}, Cd^{2+}, Cu^{2+} etc that determine the toxicity of water. Heavy metals are very harmful because of their non-biodegradable nature, long biological half-lives and their potential to accumulate in different body parts. (Monu A., et all, 2008)

Land application of waste material that may improve crop production is a very usual practice. This practice can also degrade the environment by introduction of some potentially harmful substances such as traces of heavy metals into the soil (Dowddy, R.H., et all 1986). Heavy metals have been applied to soil together with pesticides, as plant nutrients and as a constituent of waste products.

Nickel and nickel compounds have many industrial and commercial uses. Most nickel is used for the production of stainless steel and other nickel alloys with high corrosion and temperature resistance. Nickel metal and its alloys are used widely in the metallurgical, chemical and food processing industries, especially as catalysts and pigments. The nickel salts of greatest commercial importance are nickel chloride, sulphate, nitrate, carbonate, hydroxide, acetate and oxide [Grandjean P., 1984 and Clarkso N.T.W., 1988].

Natural sources of atmospheric nickel levels include wind-blown dust, derived from the weathering of rocks and soils, volcanic emissions, forest fires and vegetation. Nickel finds its way into the ambient air as a result of the combustion of coal, diesel oil and fuel oil, the incineration of waste and sewage, and miscellaneous sources [Clayton G.D., Clayton F.E., 1994; Grandjean P., 1984]. Environmental sources of lower levels of nickel include tobacco, dental or orthopaedic implants, stainless steel kitchen utensils and inexpensive jewellery (Cempel M., and Nikel G., 2005). The major sources of nickel pollution in aquatic ecosystems are domestic wastewater effluents. Nickel is easily accumulated in the biota, particularly in the phytoplankton or other aquatic plants, which are sensitive bioindicators of water pollution. It can be deposited in the sediment by such processes as precipitation, complexation and adsorption on clay particles and via uptake by biota. In soil the nickel is downloaded from industrial and agricultural activities, from sewage sludge and landfill. (Nriagu J.O., and Pacyna J.M, 1988).

The nickel exposure is frequently responsible for allergic skin reactions. Nickel hypersensitivity also causes asthma, conjunctivitis, inflammatory reactions to nickel-containing prostheses and implants, and systemic reactions after parenteral administration of nickel-contaminated fluids and medications. The sensitivity to nickel would emphasise the need to monitor nickel content in drinking water and nickel-allergic subjects should be aware of the increased absorption when drinking water on an empty stomach (Niels EN G.D., and al., 1999). Epidemiological investigations and experimental studies have demonstrated that nickel metal dusts and some nickel compounds are extremely potent carcinogens after inhalation but also that the carcinogenic risk is limited to conditions of occupational exposure (Cempel M., and Nikel G., 2005).

The maximal limit concentration for Ni^{2+} is 0.5ppm in Germany and Romania, 2 ppm in Switzerland and 3.98 pp in US. (Xiong C., and Yao C., 2011)

For obtaining the potable water with quality according to European legislation is necessary to apply adequate methods to remove the heavy metals. For removal of Ni^{2+} from water can used same methods such as: coagulation, chemical prepicitation, slow sand filters membrane, technologies, adsorption, biosorption and ion exchange resins. The last three are potential alternatives for aqueous solutions.(God, F., and Pehnivan E., 2006). In this study we used for removal of Ca^{2+} and Ni^{2+} from water Purolite S 930.

Purolite S-930 is a macroporous copolymer (styrene-divinylbenzene) based chelating resin, with iminodiacetic groups designed for the removal of cations of heavy metals from industrial effluents. (Purolite, 2011) These cations may be separated from high concentrations of univalent cations (typically sodium) and also from common divalent cations (such as calcium). Removal can be achieved both from weakly acidic and weakly basic solutions depending on the metals to be removed. **Purolite S-930** finds use in processes for extraction and recovery of metals from ores, galvanic plating solutions, pickling baths, and effluents even in the presence of alkaline earth metals (calcium and magnesium). Figure 1 presents the chemical structure of Purolite S930**.**

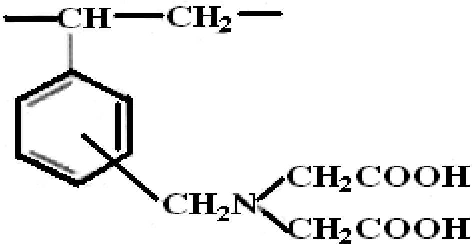

Figure 1. Chemical Structure of Purolite S930 (Deepatana A, Valix M., 2004)

The physical and chemical properties of the resin are shown in Table 1.

Table 1. Properties of commercial chelating resin (Purolite, 2011)

Polymer Matrix Structure	Macroporous Styrene-divinylbenzene
0	***1***
Functional group	Iminodiacetic acid
Particle size (mm)	0.3-1.0
Moinsture retention, H^+ range, (%)	55-65
Bed density(g/L)	710-745
Specific Grafity, Moinsture, H^+ form (g/cm^3)	1.17

0	*1*
Moisture content	
Operating temperature, max (°C)	70
pH range (operating) -H^+ form -Na^+ form	 2-6, 6-11
Total exchange capacity (meq/g wet) -H^+ form -Na^+ form	 1.52, 1.29

In this paper the equilibrium and kinetic sorption of Ca^{2+} and Ni^{2+}on ion exchange resins S930 are presented. Sorption of Ca^{2+} and Ni^{+2} on S930 was studied as a function of pH, at different concentrations of support electrolyte. Simultaneous sorption of Ca^{2+} and Ni^{2+} from their bicomponent sistems has been studied, the ratios of two metals in the binary systems Ca^{2+} : Ni^{2+} being1:2, 1:1, 2:1 and 5:1.

II. EXPERIMENTAL

Sorption of Ca^{2+} and Ni^{2+} on ion exchange resin was studied in batch experiments, at 20.0 ± 0.1^oC in a thermostatic mixing system.

The concentration of heavy metals in the supernatant was determined by atomic absorption spectroscopy (Perkin - Elmer 1100B atomic absorption spectrometer). According to a previous kinetic study a 24-h reaction period was chosen. All measurements were run in duplicate. The reported values represent the average values. In all the sorption experiments the solid/liquid ratio was 1g/L. Monocomponent and bicomponent synthetic aqueous solutions were prepared using analytical –reagent-grade $CaCl_2$ and $NiCl_2$ $6H_2O$ (all p.a. Fluka) dissolved in water. For echilibrium studies the initial concentration of Ca^{2+}varied between 14.43 and 146.7 mg/L and of Ni^{2+} between 19.95mg/L and 187.8mg/L. The isotherms are presented in Figure 2.

The adsorption capacity (a) of the resin per mass unit was calculated from the following equation:

$$a = (C_iV_i-C_eV_f)/m,$$

where: a = metal uptake, mg/g; C_i = ion concentration in the initial solution, mg/L; V_i = initial volume of solution, L; C_e = ion concentration at equilibrium in the final solution, mg/L; m = mass of dry resin used, g, (Stefan D. S. et all 2010).

The effect of the pH solution on the uptake of Ca^{2+} and Ni^{2+} was studied and the data are presented in Figure 3. The pH was varied within the range 3.96 to 6.5. The initial concentrations of metals ions in system were 58.52 mg/g for Ca^{2+} and 79.8 mg/g for Ni^{2+}. The desired pH was controlled using the suitable buffer solution (Merk, titrisol).

Simultaneous sorption of Ca^{2+} and Ni^{2+} from their binary mixed solutions was studied, and the ratios of two metals in the binary systems was 1:2, 1:1, 2:1 and 5:1. For appreciating the sorption selectivity of resin for nickel and calcium ions was using separation coefficient, $\alpha_{Ni/Ca}$, given by equation:

$$\alpha_{Ni/Ca} = \frac{\dfrac{a_{Ni}}{a_{Ca}}}{\dfrac{Ce_{Ni}}{Ce_{Ca}}} = \frac{a_{Ni} \cdot Ce_{Ca}}{a_{Ca} \cdot Ce_{Ni}}$$

where: a_{Ni} and a_{Ca} are lead and calcium ion concentrations respectively, in solid phase, mg g^{-1}; Ce_{Ni} and Ce_{Ca} are nickel and calcium ion concentrations respectively, in liquid phase, mg·L^{-1}. If α > 1 the resin exhibits selectivity for PB cations, while for α < 1 the resin exhibits selectivity for Ca cations, [Neagu, V, 2007]. The variation of separation coefficient, $\alpha_{Ni/Ca}$, with pH at different ratio Ca^{2+}/Ni^{2+} was presented in Figure 5.

III. RESULTS AND DISCUSSION

According to a previous kinetic study, Figure 2, one can notice that the contact time for all experiments was chosen 24 hours for reaction period. By comparing the isotherms of adsorption for Ca^{2+} and Ni^{2+} of S930 in the same initial conditions at variable initial concentrations (Figure 3), one observe the increasing of adsorption capacity with increasing of the initial heavy metal concentration. The S930 has a higher uptake capacity for Ni^{2+} than for Ca^{2+} with the values 37.16 mg/g 11.43 mg/g, respectively.

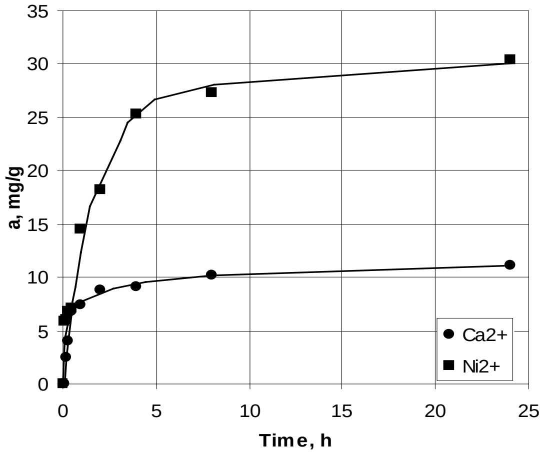

Figure 2. The variation of Ni^{2+} and Ca^{2+} ions concentration sorbed on S930 in time, T = 20 ± 0.5ºC, pH =6.0 ± 0.02, C_B=1g/L

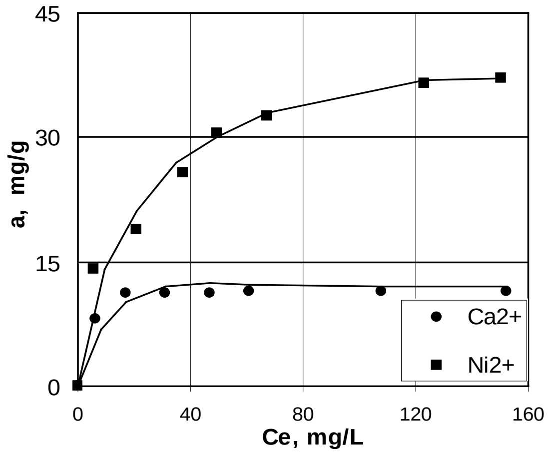

Figure 3. Sorption isotherms of Ca^{2+} and Ni^{2+}on S930 resin
T = 20 ± 0.5ºC, pH =6.0 ± 0.02, C_B=1g/L

The pH value of the solution influences the metal ions Ca^{2+} and Ni^{2+} sorption capacity, results are showed in Figure 4. At pH increased, the proton concentration inside the aqueous medium is lowering and the processes of hydroxyl and carboxyl active group dissociation are intensified, and thus the Ca^{2+} and Ni^{2+} cations can be more easily bound on the resin active centres.

The variation of separation coefficient, $\alpha_{Ni/Ca}$ with pH at different ratios Ca^{2+}/Ni^{2+} is presented in Figure 5. From these diagrams one can see that the S930 resin has a higher selectivity for Ni^{2+} comparatively to Ca^{2+} in all systems studied, the increasing of nickel concentration inside the aqueous medium results in increasing its uptake on S930 resin.

The increasing of pH values has a positive influence of nickel selectivity, the resin affinity for nickel increasing. The maximum value of separation coefficient, 5.96, was obtained for a ratio $Ca^{2+}/Ni^{2+}=5/1$ in binary system at 6.5 value of pH.

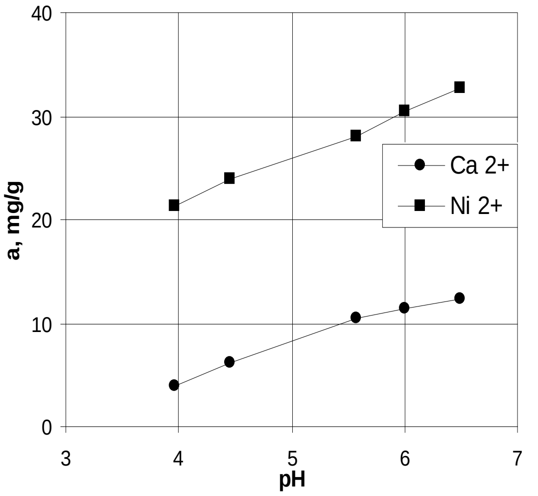

Figure 4. The influence of pH on Ca^{2+} and Ni^{2+} sorption by S930 resin
T = 20 ± 0.5ºC, C_i for Ca^{2+} =58.52 mg/L a for Ni^{2+} = 79.8mg/L; C_B=1g/L

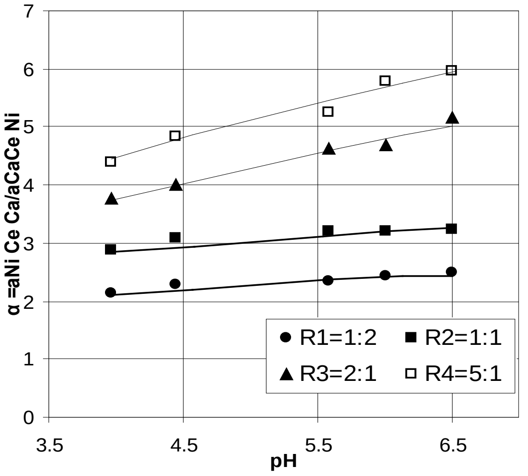

Figure 5. The influence of the solution pH on the separation coefficient values for Ni^{2+} /Ca^{2+} in binary system for S930 resin

IV. CONCLUSION

The kinetic study performed on S930 resins showed that the time necessary for equilibrium of sorption of calcium ions is the same for both studied resins. Therefore, 24 h were considered sufficient time to reach heavy metal adsorption equilibrium

The sorption isotherms indicate a greater affinity of S930 for Ni^{2+} cations, compared to the Ca^{2+} ions.

The increase in pH of the solution has a positive influence on the sorption capacity for both studied ions.

During the competitive sorption on the S-930 resins of binary systems a higher selectivity for nickel ions was observed compared to calcium ions, the separation factor ($\alpha_{Ni/Ca}$) being much higher than unite.

V. REFERENCES

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