Sorption of Ni$^{2+}$ Ions by Anion Exchangers based on Epichlorohydrin Oligomers and 4-Vinylpyridine

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I. Introduction

The problem of extracting Ni$^{2+}$ ions is an actual when purifying wastewater of mining and metallurgical and engineering industries from them for example, when processing copper-nickel ore [1], sewage of nickel plating plants [2, 3] and others. Nickel is widely used in technology as anti-corrosion coatings, it is part of many non-ferrous alloys [4]. Production of nickel from oxidized nickel and sulfide ores is accompanied by formation of large amounts of waste water, which leads to water pollution [5]. Thus, the coefficient of accumulation of nickel by hydrobionts (the ratio of concentration of pollutants in the organism of a hydrobiont to its concentration in the aqueous medium) reaches 85-235.

In this regard, high requirements to methods of its removal from industrial wastewater are obvious. One of the promising methods for separation and concentration of microquantities of elements is the sorption extraction from solutions by polymer complex forming sorbents [6,7]. Therefore, an actual objective is to obtain ion exchangers based on the available materials and having high sorption properties with respect to nickel ions.

An important direction in practical application of ion exchange materials is purposeful synthesis of new selective sorbents and improvement of characteristics of known synthetic materials by introduction (into the sorbent matrix) of functional groups capable of reacting with metal ions to form complexes and chelates or ion associates.

II. Experimental

a) Reagents and materials

Epichlorohydrin (ECH) (99 %, empirical formula C$_3$H$_5$ClO, Mw 92.52 g mol$^{-1}$, density 1.183 g/ml at 25°C, boiling point 115-117°C, melting point -57°C, refractive index n 20/D 1.438 Sigma-Aldrich, Germany).

4-vinylpyridyne (VP) (95 %, Empirical formula C$_7$H$_7$N, Mw 105.14 g mol$^{-1}$, density 0.975 g/ml at 25°C, boiling point 62-65 °C, refractive index n 20/D 1.549 Sigma-Aldrich, Germany).

Benzoyl peroxide (BP) (Linear formula (C$_6$H$_6$CO)$_2$O$_2$, Mw 242.23g mol$^{-1}$).

Nickel (II) sulfate heptahydrateNiSO$_4$$\cdot$7H$_2$O.

Epichlorohydrin oligomer (ECHO) was obtained in the presence of the M-14 catalyst, activated aluminosilicate (H$^+$ + Al$^3$+), taken in an amount of 1% of the monomer weight. The reaction mixture was heated for 2 h at 30 - 50°C and for 5-6 h at 60-80°C with stirring at a constant rate and then cooled down. The reaction product was dissolved in benzene, precipitated with water-ethanol mixture (2:1), and filtered off. The resulting viscous brown product was dried at room temperature under vacuum to constant weight.

Anion exchange resin was synthesized in an optimal condition by polycondensation of epichlorohydrin oligomer (ECHO) and 4-vinylpyridine (VP) in the presence of 0.1-0.5 wt.% benzoyl peroxide at 80 °C for 5 hours in a weight ratio ECHO:VP equal to 10:4. Then the reaction mixture is cured at 120°C for 16 hours. It was then ground to give a particle size of 0.5-1.0 mm. As a result, a new anion exchanger ECHO-VP was synthesized.
b) Study of the sorption of nickel (II) ions by anion exchangers

For preparation of model solutions the salt NiSO₄·7H₂O of analytical grade was used qualification. The concentration of nickel sulphate solutions varied from 0.165 to 2.099 g/L and the acid - in the range of pH from 1.5 to 6.9 with addition of 0.1N H₂SO₄ solution or NaOH. The contact of sorbents with NiSO₄ solution ranged from 1h up to 7 days. Sorption capacity (SC) was calculated from the difference between the initial and equilibrium concentration of the solutions, which were determined by classical polarography on the background of 0.5 M NH₄Cl on waves recovery Ni²⁺ (E₁/₂ = −1.07V).

III. RESULTS AND DISCUSSION

The effect of concentration and pH of model solutions of NiSO₄ and their contact time on sorption of Ni²⁺ ions by new anion exchangers based on epichlorohydrin oligomer and 4-vinylpyridine (Fig.1-3) was studied.

Figure 1: Isotherms of Ni²⁺ ions sorption by anion exchangers OECH -VP-I (1) and OECH -VP-II (2), the contact time is 7 days.
As is seen in Figure 1, anion exchanger OECH-VP-I absorbs Ni$^{2+}$ ions much better than OECH-VI-II, which is consistent with their values of SEC. When extracting them from NiSO$_4$ solution containing 2.1 g/L of nickel, the SC is for them respectively 346.4 and 276.0 mg/g.

One of the important factors influencing the sorption characteristics of ion exchangers is acidity of solutions. The maximum absorption of Ni$^{2+}$ ions by anion exchanger OECH-VP-I was observed at pH 5.2 (Fig. 2). As follows from Fig. 3, it takes 6 hours to reach the equilibrium state between the anion exchanger OECH-VP-I and a solution of NiSO$_4$, containing 2.1 g/L of nickel and having pH 5.2.

The authors [8] in the study of the sorption of Ni$^{2+}$ ions from solutions, containing 100 mg/L (pH 5.5), by industrial weak basic anion exchangers AV-17, AM-7 and AN-221 stated that their SC is respectively 0.021, 0.162, 0.219 and 0.278 mg-eq/g.
When extracting Ni\(^{2+}\) ions from 0.005 N solution of the mixture of copper, nickel and cobalt sulfates by anion exchangers based on allyl bromide, OECH and polyethyleneimine or polyethylenepolyamine, SC by Ni\(^{2+}\) ions reaches 0.67 mg-eq/g [1]. The exchange capacity of the polyelectrolyte based on glycidyl methacrylate and poly-2-methyl-5-vinylpyridine by nickel does not exceed 45 mg/g or 1.53 mg-eq/g [9].

Sorption characteristics of anion exchangers are known [6,7] to depend on the concentration of solutions. It was found that, when extracting Ni\(^{2+}\) ions from NiSO\(_4\) solutions containing 0.16; 0.50 and 2.10 g/L, SC of anion exchanger OECH-VP-I is respectively 2.32; 4.61 and 11.80 mg-eq/g. Comparison of the results with the literature data shows that the SC of synthesized anion exchanger based on OEHG and 4-vinylpyridine is much higher than that of the known and industrial anion exchangers.

It is known [10] that the topological structure given by the chemical structure of the initial monomers and the synthesis conditions plays an important role in shaping the properties of cross-linked polymer. The affinity to the anion exchange resins of complexing metal ions depends on their porosity and electron donating capability of the functional groups [11]. Fig. 4 shows the surface morphology of the anion exchanger OECH-VI-I. These electron microscopic analyses showed the anion exchanger at OECH-VI-I it is presented in the form of straight folds.

The anion exchanger has a developed system of macropores. As seen from Fig. 4 their sizes OECH-VI-I are within 0.698-1.764 microns, and the individual pores reach 2.585 microns. Consequently, high sorption capacity of the anion exchanger OECH-VI-I apparently due to its surface microstructure more precisely and greater porosity.

Figure 4: Microstructure surface of anion exchanger OECH-VI-I
IV. Conclusion

The sorption activity of new anion exchangers based on oligomers of epichlorohydrin and 4-vinylpyridine towards nickel (II) ions were studied, looking into the dependency on the concentration and pH of the model solutions of Nickel (II) sulfate heptahydrate, and the contact time. It was established that it has a high sorption and good kinetic properties with respect to the nickel (II) ions when extracting nickel (II) from the individual solutions. It was found that at a pH of 5.2 the SC of the ECHO-VP-I anion exchanger reaches maximum values of 346.4 mg/g respectively.

References Références Referencias
