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

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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.

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In this study, we synthesized and characterized of anion exchangers OECH-VP-I and OECH-VP -II based on epichlorohydrin oligomer (ECHO) and 4 – vinylpyridine (VP).

II. Experimental

a) Reagents and materials

Epichlorohydrin (ECH) (99 %, empirical formula C_3H_5ClO, 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_7H_7N, 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 $(C_6H_6CO)_2O_2$, Mw 242.23g mol^{-1}).

Nickel (II) sulfate heptahydrate$NiSO_4{\cdot}7H_2O$.

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 washeated 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 optimalcondition by polycondensation of epichlorohydrin oligomer (ECHO) and 4-vinylyridine (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-4VP was synthesized.Thespatialstructureoftheanionexchangerresin:

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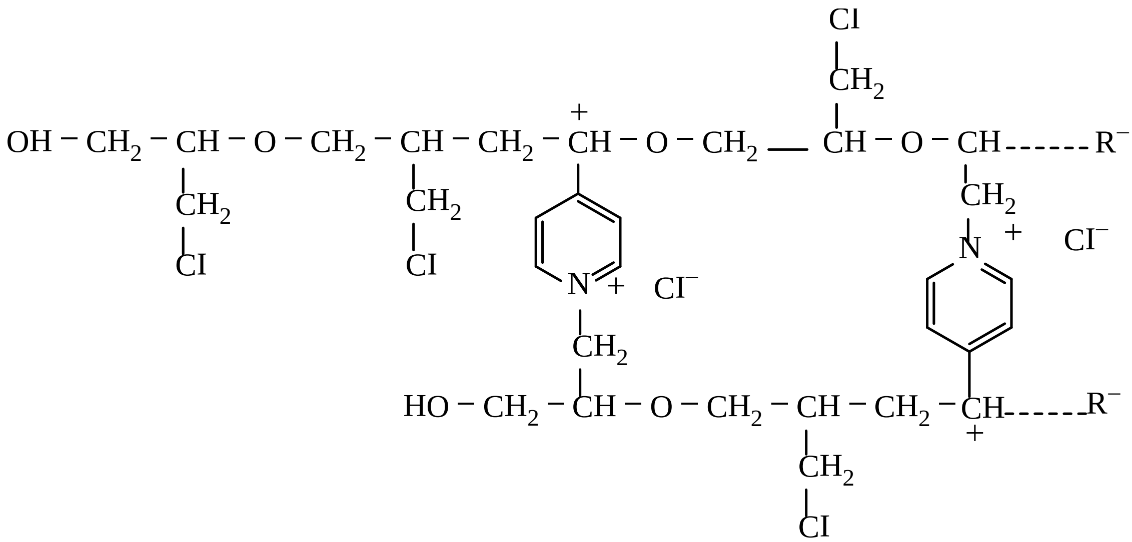

b) Study of thesorption of nickel (II) ions by anion exchangers

For preparation of model solutions the salt $NiSO_4{\cdot}7H_2O$ 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 H_2SO_4 solution or NaOH. The contact of sorbents with $NiSO_4$ 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 NH_4Cl on waves recovery Ni^{2+} ($E_{1/2} = -1.07V$).

III. Results and Discussion

The effect of concentration and pH of model solutions of $NiSO_4$ and their contact time on sorption of Ni^{2+} ions by new anion exchangers based on epichlorohydrin oligomer and 4-vinylpyridine (Fig.1-3) was studied.

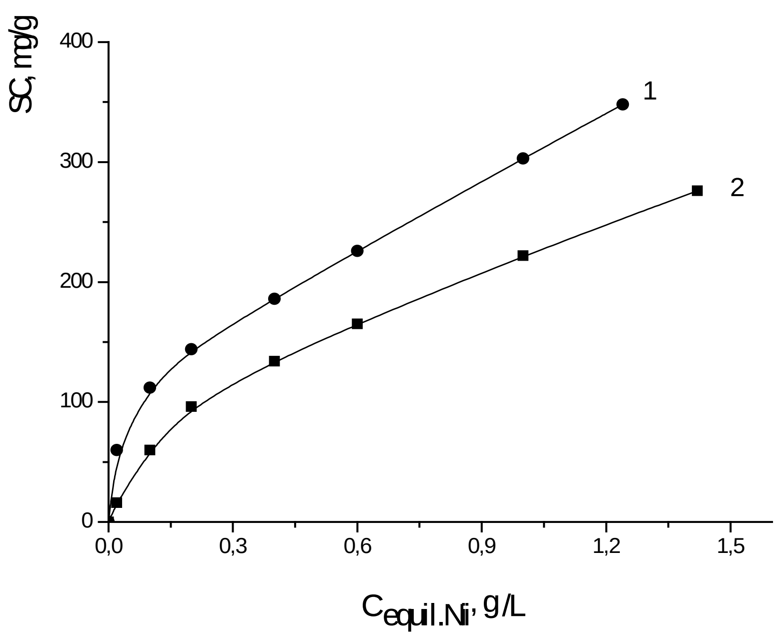

Figure 1 : Isotherms of Ni^{2+} ions sorption by anion exchangers OECH -VP-I (1) and OECH -VP-II (2), the contact time is 7 days

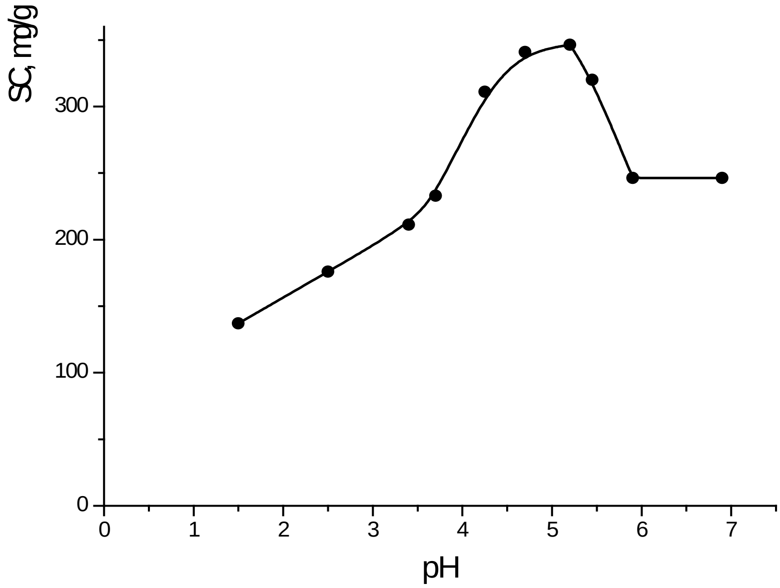

Figure 2 : Dependence of sorption of Cu^{2+} ions by anion exchanger OECH -VP-I on acidity of $NiSO_4$ solutions (C_{Ni}= 2g/L, contact time is 7 days)

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.

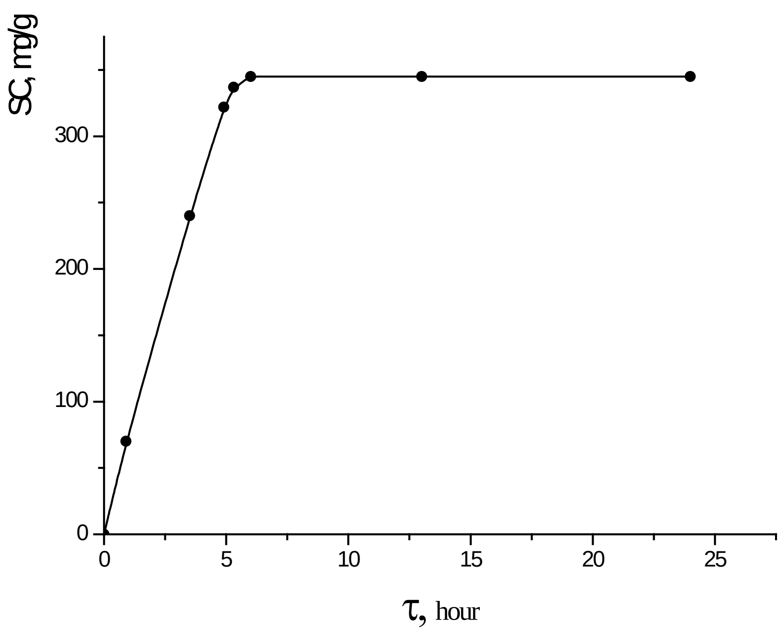

Figure 3 : Kinetic curves of sorption of Ni^{2+} ions by anion exchanger OECH-VP-I (1) from $NiSO_4$ solution (C_{Ni}=2,1g/L, pH 5.2)

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, AN-31, 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 structuregiven bythe chemical structure of the initial monomersandthe synthesis conditionsplays an importantrole inshaping the properties ofcross-linked polymer.The affinityto theanion exchange resinsof complexingmetal ionsdepends on theirporosity andelectron donatingcapabilityof the functionalgroups [11]. Fig.4shows thesurface morphology ofthe anion-exchangerOECH-VI-I. These electrons microscopic analysisshowedthe anion exchangeratOECH-VI-I it is presentedin the formof straightfolds.

The anion exchangerhasa developed systemof macropores. As seen fromFig. 4their sizesOECH-VI-I are within0.698-1.764microns, and the individual poresreach2.585microns.Consequently, high sorption capacityof the anion exchangerOECH-VI-Iapparently due toits surfacea microstructure more precisely and greaterporosity.

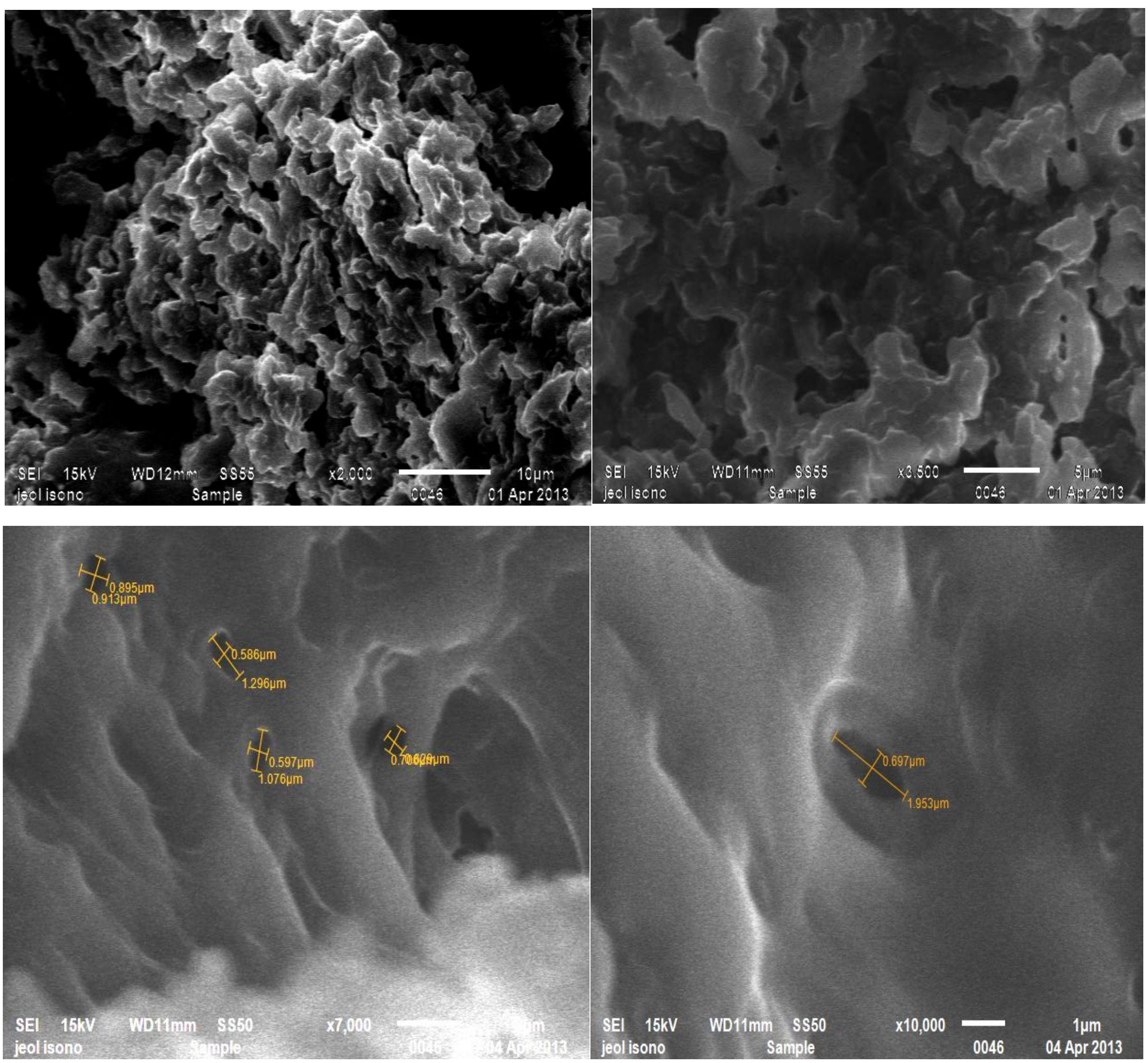

Figure 4 : Microstructuresurface of anion exchangerOECH-VI-I

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.

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