Sorption of Heavy Metal Ions by New Anion Exchanger Based on a Copolymer of Glycidyl Polyethyleneimine

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Abstract

A new polyethyleneimine nitrogen-containig exchanger network structure with static exchange capacity of 0.1 N solution of HCl 4.7 mEq/g was obtained by polycondensation of glycidyl methacrylate, styrene , acrylonitrile with polyethyleneimine. Sorption of iron(II), copper (II) and zinc (II) ions was studied and investigated in static conditions from model solutions of sulfates of copper zinc and iron, in dependence on their concentration and pH, as well as their contact time with the ion-exchanger. Found that the magnitude of the sorption capacity of the ion exchanger for ions of iron (II) at pH 1.63 significantly higher than the copper ion (II) at pH 1.62. It has been established that zinc ion (II) is absorbed best by the sorbent at pH 6.29. In these conditions the sorption capacity of the sorbent for ions iron (II), copper (II) and zinc (II) respectively equal to 1.1142 mmol / g(Fe),0.7595mmol /g(Cu)and 0.6813mmol /g (Zn). The sorption ability new nitrogen -containing anion exchanger with respect to iron (II) and copper (II) ions is significantly higher than for industrial ionite of AB-17, AC-n and ampholyte VP-14K.

Key words:Glycidylmethacrylate-styrene-acrylonitrile-polyethyleneimine(GMA-SE-AKN-PEI), sorption capacity (SC), copper sulfate, zinc sulfate, ferrous sulfate, copper (II) ions, zinc (II) ions, and iron (II) ions,

Introduction

At the enterprises non-ferrous metallurgy and metal processing industry in technological processes generated waste water contaminated with heavy metal salts, which have a very detrimental effect on the ecosystem[1]. They are persistent pollutants with a cumulative effect [2].

Many of salts in aqueous solutions formed synergistic mixtures, the toxic properties which exceed the analogous properties of the individual components. These substancesare poisonous for aquatic organisms and plants even for human at higher concentrations. For example, it was found that [3] copper and zinc compounds even at low concentrations (0.001 g / l) inhibits the development, and for large (more than 0.004 g / L) cause toxic effects on the aquatic fauna

Obtaining anion exchange materials which may be used in processes of extracting copper (II) and chromium (VI) ions in hydrometallurgy, as well aswastewater treatment and industrial water [4-5].

In this connection, development of new effective sorbent with high sorption and kinetic characteristics to extract the ions of copper (II) and zinc (II) is actual.

Goal of the work -sorption study ions ofiron(II), copper (II) and zinc (II) with new nitrogen - containing ionite which based on glycidyl methacrylate, styrene , acrylonitrile with polyethyleneimine.

Experimental

Sorption ions of Fe^{2+}, Cu^{2+} and Zn^{2+} with GMA anion exchanger-GMA-SE-AKN-PEIin OH form (grain size 0.5-1 mm) was studied in static conditions with occasional agitation and a ratio of sorbent: solution

equal to 1: 400, room temperature of 20 ± 2 °C,varying the concentration of iron in sulfuric acid solutions from 0.0884 to 0.3220 mmol / dm^3, copper from 0.0784 to 0.2620 mmol / dm^3 and zinc - from 0.0387 to 0.2891 mmol/ dm^3.The contact with the sorbent solution was 7 days.For the preparation of solutions were used salt $FeSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$ and$ZnSO_4 \cdot 7H_2O$ with the qualification of "ch.p".

Sorption capacity (SC) was calculated from the difference between the initial and the equilibrium concentration of the solutions, which were determined by atomic absorption spectrometry (Shimadzu AA-6200).

Structure of the surface anion exchangers was studied by electron microscopy with a scanning microscope JSM 6510LA company JEOL (Japan) at a resolution of the microscope 30 $Å \cdot cm^{-1}$.

Results and Discussion

Task of creating a high-quality materials and high-performance ion exchange processes could be settled only in a detailed study of sorption of metal ions depending on the conditions of the process, that is, as the equilibrium and kinetic properties of ion exchangers.

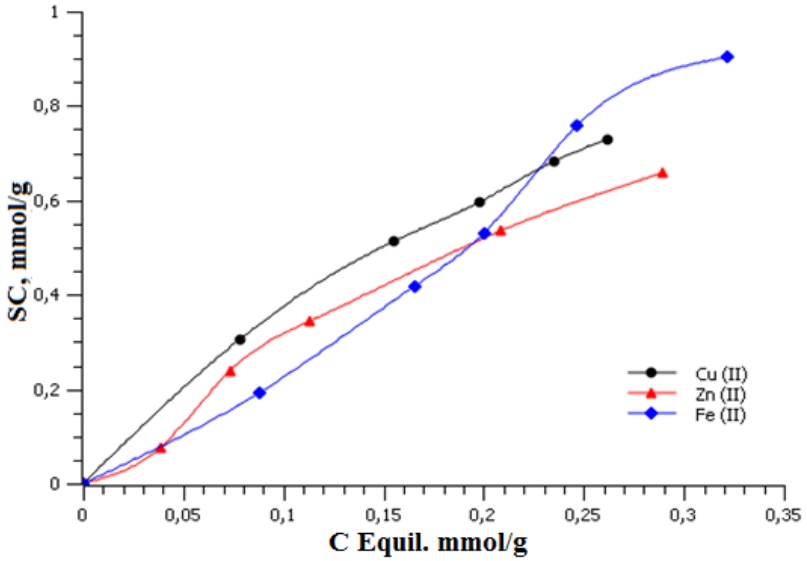

Fig. 1. Sorption isotherms of iron ions (II) from $FeSO_4$ solution (pH 1.63), copper ions (II) from $CuSO_4$ solution (pH 1.62) and zinc ion (II) from $ZnSO_4$ solution (pH 6.29)with the anion exchanger of GMA-SE-AKN-PEI,The duration of the contract 7 days.

Analysis of sorption isotherms (Fig.1) showed that with an increase in iron (II), copper (II) and zinc (II) in solutions of $FeSO_4$, $CuSO_4$ and $ZnSO_4$ sorption capacity of the anion exchanger GMA-SE-AKN-PEI, for iron ions (II) reachesed from 0.1937 to 0.0936 mmol / g, copper (II) increases from 0.3061 to 0.7284 mmol / g,and zinc ions (II) sorption capacity increased from 0.0764 to 0.6576 mmol / g. With the reduction of iron (II), copper (II) and zinc (II) in solutions of $FeSO_4$, $CuSO_4$, and $ZnSO_4$ degree of extraction for ions of iron (II) climbed from 65.5 to 97.29% and copper (II) with an ion exchanger of GMA-SE-AKN-PEIincreased from 74.15 to 98.05%and by ions of zinc (II) degree of extraction surged from 37.6 to 97.43%.

Optimum condition sorption process are determined by along with other factors by protonating the functional groups of the ion exchanger and hence the pH.With dropped of solution's pH from 6.2 to 1.6 sorption capacity of the ion exchanger GMA-SE-AKN-PEIby iron and copper ions rose, reaches a

maximum value 1.1142 mmol / g at pH 1.63 (Fe) and 0.7595 mmol / g at pH 1.62 (Cu).The highest zinc ions sorption was observed at pH 6.29 with the ion exchanger SC equals 0.6813 mmol / g (Fig. 2). By reducing the acidity to pH 1.57 CE is decreased by ions of zinc (II) to 0.1739 mmol / g.

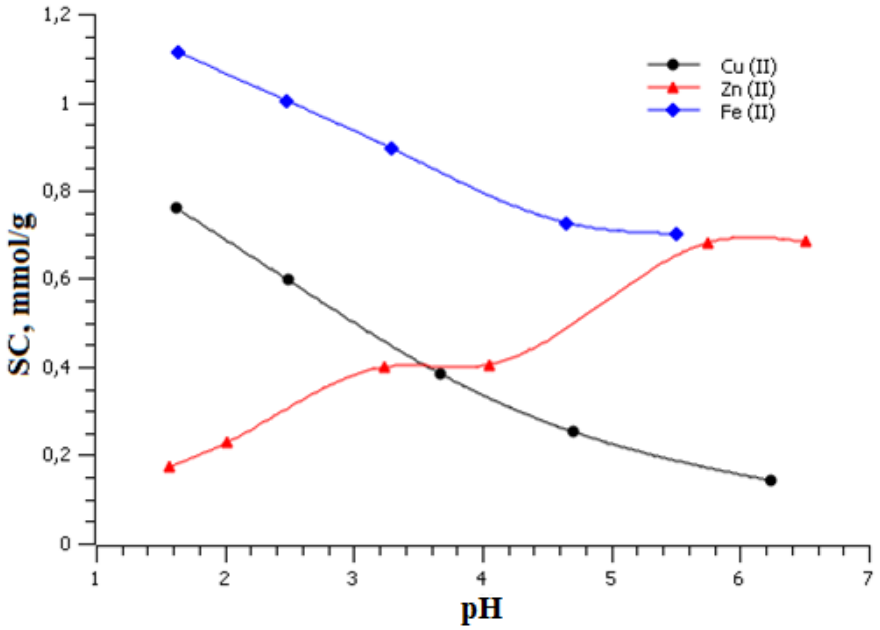

Fig. 2 The dependence of the sorption ions of iron (II) from $FeSO_4$(C_{Fe}= 0,3220mmol /dm^3) copper ion (II) from solution of $CuSO_4$ (C_{Cu}= 0,2620mmol / dm^3) and zinc ion (II) from $ZnSO_4$ (C_{Zn}=0,2891 mmol / dm^3) with the ionite of GMA-SE-AKN-PEIfrom acid medium. The duration of the contract 7 days.

The maximum sorption capacity of ionite for the ions of iron(II), copper (II) and zinc (II) is explained at the given pH, probably, that along with the ion exchange takes place complexation owing to the presence in its structure of the atoms of nitrogen and oxygen with a lone pairs of electrons due to donor-acceptor interaction. Wherein the zinc cationZnO^+, which is formed in acidic medium could be formed complexes with oxygen atoms of simple ether and hydroxyl groups which also available in structure of the GMA-SE-AKN-PEI-ionite that is well known, Zn^{2+} bond stronger than nitrogen atoms. That fact, the decrease of pH solutions leads a significant decline in the sorption of such cations, like Fe^{2+}, Cu^{2+}generated as a result of possible reduction of iron (II), copper (II), it explains that the complexes formed by reacting of iron (II), copper (II) with amino groups ion exchanger, destroyed by reducing the acidity.

A study of the kinetic properties of GMA-SE-AKN-PEI –ionite showed that equilibrium state for the sorption of copper ion (II) and zinc (II) is achieved respectively 3 and 0.5 hours, whereas the equilibrium between these solutions and AM-p anion exchangers, AM-pand ampholytePI-14K were achieved only when the contact time about 5 hours (Fig. 3)

The obtained kinetic dependences shows that the implementation of industrial process wastewater treatment from iron, copper and zinc ions loading apparatus by using anion exchanger GMA-SE-AKN-PEImay be 2-2.5 times less than using the AM-p anion exchangers, AM-pand ampholyte PI-14K. In this way, In this way, on the basis of research it can be concluded that the new nitrogen -containing anion resin GMA-SE-AKN-PEI is promising for the sorption of iron(II), copper (II) and zinc (II) ions, It exhibits with high absorption ability, than industrial AM-p anion exchangers, AM-p and ampholyte PI-

14Kand it can be implemented process of wastewater treatment enterprises which contain ions of iron, copper and zinc.

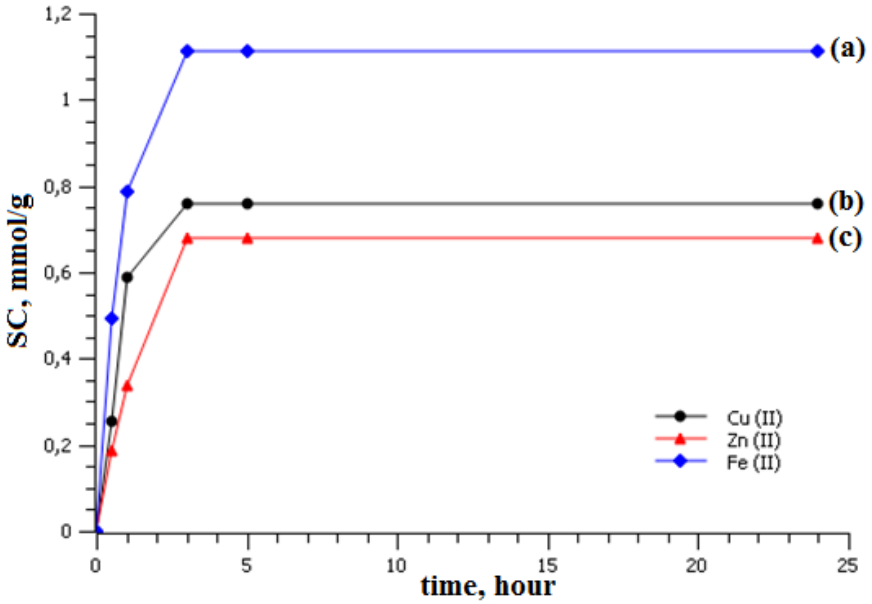

Fig. 3. Kinetic curves of sorption of ions iron(II)(a), copper (II) (b) and zinc (II) (c) using polymer GMA-SE-AKN-PEIfrom $FeSO_4$ (C_{Fe}= 0.3220mmol / dm^3, pH 1.63), $CuSO_4$ (C_{Cu}= 0.2620mmol / dm^3, pH 1.62) and $ZnSO_4$ (C_{Zn}=0.2891 mmol / dm^3, pH 6.29).

Fig. 4 the morphology of the surface of theGMA-SE-AKN-PEI-anion exchanger was shown.These electronic microscopic analysis shows the structure of the GMA-St-DCA-PEI anion exchanger's surface is presented in the form of coral surface. Anion exchanger have developed system of macropores.As can be seen from Fig.4 their sizes range from 2,263 to 8,720 microns. Consequently, increased sorption capacity of anion exchanger of GMA-SE-AKN-PEIobviously, microstructure due to its surface, more precisely, greater porosity.

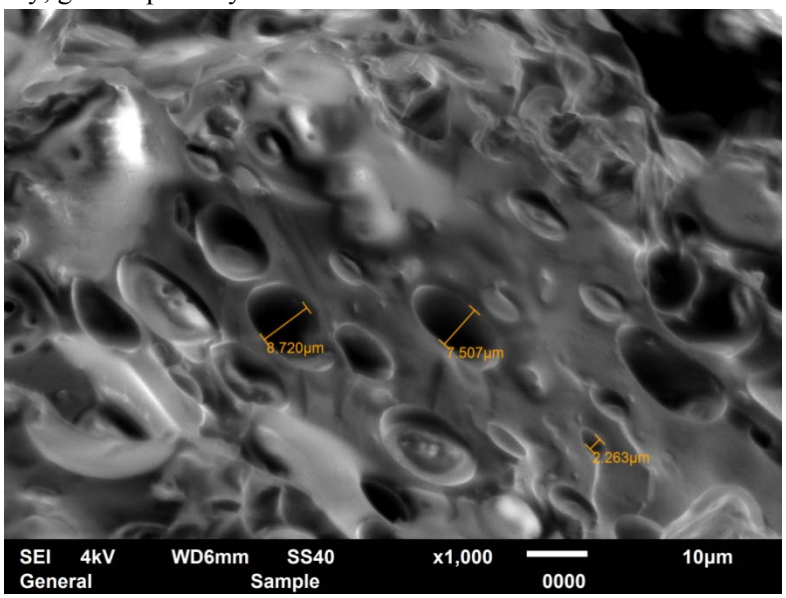

Fig. 4. The microstructure of the surface of anion exchanger GMA-SE-AKN-PEI

Conclusions

Sorption process of iron (II), copper (II) and zinc (II) –ions with new nitrogen-containing ionite was studied whichsynthesized modification of terpolymer of glycidyl methacrylate, styrene and acrylonitrile with polyethyleneimine with static exchange capacity 0.1 N solution of HCl 4,4 meq / g.

It is found that the optimal conditions of the exchange capacity for ions of iron, copper and zinc reached respectively 1.1142 mmol/g (Fe), 0.7595 mmol/g (Cu) and 0,6813 mmol/g (Zn).

It has been established that its sorption and kinetic properties with respect to iron(II), copper ions (II) and zinc (II) with the new ion-exchanger has high index and significantly higher than that of industrial ion exchangers of AB-17, AM-p and ampholyte PI-14KThus, it is shown that the new macroporous anion exchangers have selective properties and which be used for separation of cation ionsof Fe^{2+} , Cu^{2+} from Zn^{2+} ions.

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