Perspective Wastewater Treatment from Cu²⁺ Ions in the Mining Industry

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Abstract. The synthesis of new cation-exchanger based on local raw materials for the extraction of copper from copper-containing solution investigated. A review of the literature regarding the problem of ion exchange method and the use of mine wastewater treatment process is presented. Sorption selectivity of Cu²⁺ ions by cation exchanger in the H- and Na-forms from dilute solutions was studied in the target concentration range 90 mg/dm³ and 5,49 g/ dm³. The full dynamic exchange capacity calculated. The cation exchanger analyzed with consideration for IR spectroscopic, chemical analysis, and scanning electron microscopic data. Quantum-chemical calculations performed that synthesized cation-exchanger stable complexes with Cu²⁺ ions. Obtained cation exchanger due to excellent behavior recommended removing copper ions from wastewater in the mine industry.

1 Introduction

When developing ore deposits, one of the main components of environmental damage is its pollution with heavy metals, which spread in it in various forms, mainly with surface and groundwater. Heavy metals, as is known, can have an inhibitory effect on the flora and fauna, starting with soil microorganisms. For example, copper, zinc, silver in the form of simple ions (in this case, cations) in soil waters sharply inhibit the activity of nitrogen-fixing bacteria, and, accordingly, worsen the conditions of soil nutrition for higher plants and further along the food chain - fauna. However, they are especially sensitive to the presence of high concentrations of heavy metals in the aquatic environment, their immediate inhabitants - fish and freshwater mollusks.

In the wastewater of mining enterprises, the content of these metals exceeds the maximum permissible concentration (MPC) on orders, for example, on zinc excess MPC can reach 400 times. With the volume of discharge into the environment of liquid waste, having tens of millions of order m³/year. Only in the processing of copper and copper-zinc pyrite ores the extent of environmental pollution by copper, zinc and the accompanying cadmium is determined by areas of thousands of square kilometers.

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1.1 Literary analysis of mine water treatment methods

The recovery of metals from sulfide-rich ore bodies proceeds through a series of steps: from mining to crushing to mineral recovery, followed typically by smelting of the sulfide ores, and thence to metal refining; although the nature of the ore body dictates the processes used to extract metals from ore, each of these steps generates a waste stream. The volumes of the waste streams can be large. For example, production of 1 t of copper typically requires the excavation and processing of 100 t of rock. Each of the steps of metal production can lead to the generation of low-quality water [1].

The present study [2] focused on the reprocessing of copper and nickel from mine tailings. In this work, recovery of copper and nickel from mine tailing by combined process of flotation and high pressure oxidative leaching were considered. In the first stage, effects of flotation parameters including collector type, collector dosage, and pH and pulp density were examined. The results showed that over 80% copper recovery was achieved under the optimized flotation conditions while nickel recovery was lower than 30% due to its co-existence with gangue minerals of pyrrhotite, pyrite and other clay minerals. In the second stage, key parameters, particularly concentration of sulfuric acid, temperature, pressure and leaching time were investigated to test the leaching efficiency of copper and nickel from the flotation concentrate with high pressure oxidative leaching (HPOL). A comparison was made between the leaching efficiencies of copper and nickel from flotation concentrates and mine tailing. This method requires special reagent preparation of mine water, which includes the addition of flotation agent.

Reverse Osmosis is used to remove heavy metals with a pressure-driven membrane separation process with the function of a concentration gradient. The contaminant water is pumped across the membrane with pressure, which aids in the removal of heavy metals [3]. A common disadvantage of reverse osmosis schemes is the need to dispose of the concentrates from the reverse osmosis unit, which can be neutralized only by evaporation to obtain dry salts.

The most effective technology for cleaning mine water is the ion exchange method. Ion exchangers show good selectivity with respect to metal ions. It depends largely on the structure of the polymer and specifically on the ionic radius and ionic charge density of the metal ions. An ion of higher charge density tends to displace an ion of smaller charge density. Trivalent ions are preferentially adsorbed, then divalent ions. Within ions of the same charge selectivity is governed by bond strength. This is determined by the electrovalent characteristic of the metal ion. Metal ions which are more electrovalent bind more strongly and are preferentially adsorbed. For example, copper is more electropositive than zinc; as a result, from an effluent containing dissolved copper and zinc, cupric ions are preferentially adsorbed.

KAB is not a thermodynamic quantity. It is a rational selectivity coefficient used to quantify the performance of one ion over another. Usually it is expressed on a relative scale with a "standard" cation as the base [4].

The aim of the study is to clean mine waters from heavy metals, mainly copper, as well as hardness salts of calcium and magnesium using a synthesized ion exchanger [5].

1.2 Synthesis of Ion-Exchangers polymerization type

Ion-exchange resins are generally made from methacrylic acid, sulfonated styrene, and divinylbenzene (DVB).

Cation exchangers are anionic polymers that contain carboxyl or sulfate groups with hydrogen, potassium, and sodium as counterions. Cation exchangers with weak acidity are made from a polymer of methacrylic acid (containing COOH) cross-linked by DVB. The

counterion of the acidic carboxyl group is either hydrogen (as in polacrilex resin) or potassium (as in polacrilin potassium). To make a cation-exchange resin with a stronger acidity, water-insoluble styrene is used to prepare the polymer, which is sulfonated to make it hydrophilic. DVB is also used to cross-link the polymer, and the counterion of the sulfate group (SO3) is generally sodium [6].

1.3 Synthesis of Ion-Exchangers polycondensation type

Polycondensation is another technique used to synthesize polymers. The reason for the name derives from the elimination of a molecule of water from reactants at each polymerization step. This technique may be applied to multifunctional units to produce thermoset polymers. A classical example of polycondensation leading to thermoset polymers is the copolymerization between phenol and formaldehyde. Formaldehyde is able to bridge together two aromatic rings, and since the functionality of a ring is five (one carbon is linked to the hydroxyl group) the cross-links between rings are ensured by a relatively low content of formaldehyde.

Industrial polycondensation cation exchangers are mainly derived from phenols and formaldehyde. The use instead of formaldehyde furfural and together phenols of diphenyl oxide will allow us to solve cardinally the problem of increasing the thermochemical and radiation resistance and mechanical strength of ion exchanges. From this point of view, as a polymer matrix for the introduction of ionic groups. A polycondensation product of diphenyl oxide and furfural was used [8]. The choice of diphenyl oxide instead of phenols is due to the fact that: 1) the presence of aromatic nuclei and the absence of hydroxyl groups make it possible to obtain polymers with high thermochemical resistance. 2) The molecule of diphenyl oxide contains 6 mobile hydrogen atoms, which make it possible to obtain ionite with a high content active groups; 3) The presence of an oxygen bridge between the aromatic rings promotes an increase in the selectivity to ions of certain metals; 4) Diphenyloxide is relatively inexpensive and available.

Our purpose is to provide research work syntheses of cation exchanger, with sulfonic acid groups, by sulfonation with sulfuric acid.

Until now, considering in general terms the chemical structure of polymers of different classes, we essentially talked about the structural formula of the repeating unit of the macromolecule. However, the presence of many such links in the macromolecule immediately complicates the picture. Each link in the process of an elementary act of growth of a macromolecule can join the neighboring link in different ways.

The formation of the polymer is due to the reaction of the aldehyde group of furfural with the most reactive hydrogen of diphenyloxide in the ortho- and para positions, which agrees with the data obtained from IR spectroscopic studies of the obtained polymer.

The absorption bands in the 1200-1600 cm^{-1} region in the cationite spectrum correspond to SO3H groups. The absorption bands in the 3200-3500 cm^{-1} region correspond to stretching vibrations-COOH groups. The absorption bands in the 644 cm-1 region correspond to the presence of diphenyloxide groups. The absorption bands in the 1033 cm^{-1} region correspond to the 1.2.3.4-substituted benzene ring. The absence of absorption bands in the 1670 cm-1 region indicates that furfural reacts with diphenyloxide due to its carbonyl group. The absorption bands in the region 740. 810. 870 cm-1 correspond to the vibrations of the furan ring.

2 Results and discussion

2.1 Research of properties obtained ion exchanger

The important properties of ion exchangers differ with respect to the type of applications and include:
• cation-exchange capacity
• selectivity

2.1.1. Cation-exchange capacity to Cu2+ ions under dynamic conditions

One of the evaluation methods of the cation – exchange capacity is under dynamic conditions, by circulating a surfactant solution through cation exchanger, until the surfactant concentration in the effluent becomes constant.

The process of sorption of Cu^{2+} ions under dynamic conditions was carried out according to the method [9]. Experimental studies were carried out in a glass column of 15 mm in diameter, filled with sorption materials in an amount of 5 g (size fractions 0,5-3 mm). The solution was continuously passed through the adsorbent bed from top to bottom until the adsorbent was completely saturated with the adsorbed material. The initial concentration of Cu^{2+} ions in the solution is 90 mg/dm^3 and 5,49 g/ dm^3, the sorption volume is 10 cm^3, the filtration rate is 10 m/hour

Table 1. The results of laboratory studies on the sorption of copper ions Cu^{2+} on the resulting cation exchanger from copper-containing wastewater.

The name of indicators	Unit rev.	C = 90 mg/ dm^3		C = 5.49 g / dm^3	
		H-form	Na-form	H-form	Na-form
Full dynamic exchange capacity	mol/m^3	550	703	1350	1672
Dynamic exchange capacity before reakthrough	mol/m^3	150	185	775	860
The actual consumption of the regenerating solution	g/mol	9531	7527	2500	2134
Wash water consumption	volume / volume	4	6	6	8

From the data in table 1, it can be seen that when used in the purification process of phosphate cation exchanger in the Na-form, the sorption of copper ions increases, which is consistent with the literature data. Also, the flow rate of wash water when transferring to the Na-form increases compared with the H-form.

Based on the laboratory studies, it can be concluded that the obtained cation exchanger can be used in the sorption of Cu^{2+} ions from copper-containing wastewater with a high copper content, as well as from waste waters with a low content of copper ions.

2.1.2. Mechanism of selectivity properties

The synthesis of new ion-exchange polymers based on local raw materials for the extraction of copper from copper-containing effluents is a pressing issue. It is advisable to use chemical information about their structure and properties in order to determine with the help of computer computing technologies the range of new molecules in which one can expect the manifestation of specified properties and characteristics. To do this, it is necessary to solve the quantitative relationship between the structure and activity, the structure and properties of the molecule, as well as to establish relationships that relate the characteristics of a

particular property to the known chemical properties of molecular-molecular geometry, dipole moment, charges on atoms, etc.

Quantum-chemical calculations performed in the OpenMX 3.7 software package showed that the synthesized ion-exchange polymers based on furfural and diphenyloxide form stable complexes with Cu^{2+} ions.

It should be noted that the most stable complexes in the sulfonic cation exchanger are observed between the O and $-SO_3H$ atoms.

Table 2. Measurement results.

Ion exchange polymer	Sorption energy, meV (kJ/mol)	Junction length, Å	Angle, degree
Cation exchanger	2211,36 (213,36)	Cu – O19 = 2,17 Cu – O33 = 1,90	≤(O19-Cu-O33)= 86,9

From the data of table 2 it can be seen that in the process of complexation of the cation exchanger with copper ions the length of the compounds is 2 Å.

2.2. Perspective on ion exchangers for mine wastewater treatment

The Cu^{2+} sorption efficiency depends mainly on the type, functional groups, bead size, as well as other physical and chemical properties of the ion exchanger. Functional groups can be immobilized in a polymeric matrix by chemical reaction or can be introduced by physical sorption. The resins with preselected functional groups were developed for application to hydrometallurgy processes where conventional ionic ex-changers were selected less frequently for the removal of metal ions. Resins having chelating functional groups can remove Cu^{2+} ions through a combination of ionic interactions, electrostatic interactionsand coordination and thus a higher selectivity for Cu2+. Chelating ion exchange resin in general, coordinates copolymers possessing covalently bonded side chains which contain one, two or more donor atoms [10].

To determine the perceptivity cation exchanger for mine wastewater treatment subjected to elemental analysis. The results of the experiment are shown in electronic spectra's in Fig.1.
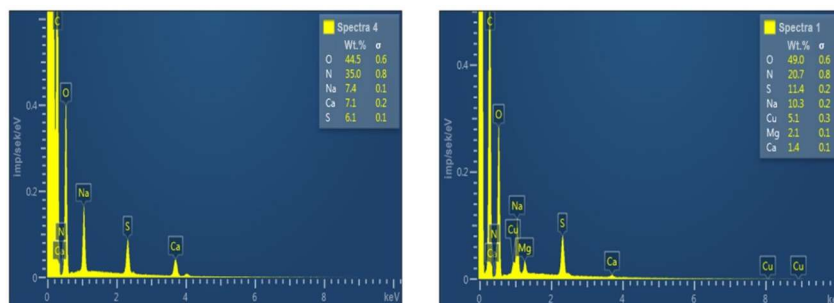

Fig. 1. Results of elemental analysis of obtained cation exchanger.

One of the most challenging aspects of treatment process design is the analysis and selection of the treatment processes capable of meeting the permit or recycling requirements. The methodology of process analysis that leads to process selection includes several evaluation steps. These evaluations vary greatly with the project and characteristics of wastewater. Nevertheless, any process analysis needs to consider several important factors: process applicability, applicable flow range and variation, reaction kinetics and reactor

selection, performance, treatment residuals and odor, sludge treatment, chemicals/polymers requirements, and energy requirements. Once process analysis is done, process selection or design commences; several methods of process design or selection may be considered— process selection based on empirical relationship from experience or literature and process design based on kinetic analysis or modeling. Chapter 1 provides the basic tools to assist the selection process [11].

The cation exchanger contained atoms of sodium, calcium, magnesium and copper, indicating selective, as well as selective properties to copper ions. Developed cation exchanger selectively remove copper ions more efficiently than can currently be done. Cation exchanger also recommended removing or recovering copper ions from wastewater in the mine industry.

3 Conclusion

Recycling of wastewater require efficient and cheap separation methods. Similarly, the raw water must be purified to a level necessary for water reuse. One very efficient method for the separation of ions from liquids is ion exchange, which has a greater utility for the treatment of wastewater than is currently realized.

The application of cation exchanger to the recovery of copper metal ions from industrial sewage is summarized. Attention is given to ways of improving the economics of recovery. One method of making the recovery processes simpler and less costly is to employ obtained cation exchanger. Because of their excellent sorption properties possible applications of cation exchanger are reviewed.

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