Research new type of cation-exchange resin for waste water treatment

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Abstract. This article presents the studies obtaining and researching new polycondensation type phosphoric cation-exchange resin. The conditions for the phosphorylation of this polymer were selected from the experiments accumulated in relation to the phosphorylation reactions of low- and high-molecular compounds. The resulting polymer had an exchange capacity for a 0.1 N NaOH solution – 5.5 mEq/g and contained 16.5% phosphorus. Based on the studies carried out, the optimal conditions for the synthesis of the styrene-furfural polymer are assumed to be: the reaction temperature is 90°C, the concentration of the ZnCl2 catalyst is 0.07 mol per mole of furfural, and the molar ratio of styrene to furfural is 1:1. There was studied an interaction of the cation exchanger in Na- and H-forms with solutions of salts of copper sulfate, nickel, cobalt, sodium chloride, calcium and uranyl nitrate. In order to elucidate the mechanism of sorption of the cations of these metals, were taken the IR spectra of the cation exchanger in the H- and Na-form, saturated with copper ions. The less dissociated phosphoric acid groups, the stronger hydrogen bond forms phosphoryl oxygen with OH-groups. Therefore, it can be expected that as the cation exchanger is saturated with sodium, the maximum of the band corresponding to the phosphorus-oxygen bond vibrations will slightly shift to longer wavelengths as a result of the destruction of the weaker hydrogen bond.

1 Introduction

It is known that ion exchange processes are widely used for softening and desalination of water, for purification of industrial wastewater from toxic elements, sorption of valuable trace elements from various solutions, in hydrometallurgy, analytical and preparative chemistry, medicine and others [1,2]. Often, ion-exchange polymers are obtained on based on expensive scarce raw materials, which limits the possibilities and scope of their application. In order to save raw materials, it is rational to production of synthetic ion-exchange polymers based on secondary material resources [3-5]. For example, based on furfural obtained from annually renewable vegetable raw materials (waste from cotton ginning, agricultural production, such as cotton husks, guzapay, corn cobs, reeds, etc.).

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Furfural can also be obtained from logging waste, sawmilling, and woodworking, components from 30 to 45% of the volume of processed wood. The choice of furfural is also due to and other factors. The presence of a heterocyclic furan core in its structure makes it possible to obtain ion exchangers with sufficiently high rates of chemical, thermal stability, and mechanical strength. In the synthesis of ion exchangers, furfural plays the role of the condensing agent and bridging agent, the amount of which can be controlled and the degree of cross-linking, which makes it possible to obtain ion exchangers with different properties.

At present, a large amount of experimental material has been accumulated for obtaining various types of phosphorus-containing ion exchangers. The study of the properties of these ion-exchange polymers made it possible to outline the main ways of their use in many fields of science and industry.

2 Materials and methods

The molar ratio of the reagent's polymer: aluminum trichloride: phosphorus trichloride = 1:2:4. The reaction was carried out at 75°C for 6 hours, after which the ion exchanger was stripped of phosphorus trichloride and washed with humidified alcohol, decreasing the concentration successively to 50, 30, 20%, and then washed with cooled distilled water until the wash water was neutral.

To determine the dynamic exchange capacity (DEC), a sample of ion exchangers from the flask was transferred into a cylinder with a capacity of 100 cm³ and a layer of ion exchangers was compacted by tapping the hard surface of the bottom of the cylinder until sedimentation ceased. The volume of the ion exchangers was brought to 100 cm³ and with the help of distilled water the ion exchanger was transferred into the column, making sure that it was drained from the column, leaving a layer with a height of 1-2 cm above the level of the ion exchangers.

The ion exchanger in the column was washed with distilled water, passing it from top to bottom at a rate of 1,0 dm³/h. In this case, the ion exchanger was washed from acid (according to methyl orange). When a working solution of 0.1 N concentration was passed through a column with ion exchanger, the filtrate was collected in cylinders with a capacity of 250 cm³.

In the second and subsequent saturation cycles, before the appearance of ions of the working solution in the filtrate (determined after the first cycle), the filtrate was collected in 100 and 250 cm³, respectively, the concentrations of the working solution. After the ions of the working solution appeared in the proportion of the filtrate, the total volume of the filtrate was calculated.

To determine the full dynamic exchange capacity, the solution was continued to flow until the concentration of the filtrate became equal to the concentration of the working solution. In this case, the saturation control is carried out by titrating the sample with an acid solution with a mixed indicator until the color changes.

The value of the static exchange capacity (SEC) for calcium, magnesium, copper, nickel, and cobalt ions was calculated for ion exchanger samples in contact with a solution of calcium, copper, nickel, and cobalt salt and a model solution for seven days. Then, according to KBr tablets were prepared and tested.

3 Results and discussion

Proceeding from this, considering it very promising in terms of achievements in the field of synthesis of ion exchangers, we used a styrene-furfural polymer as a polymer matrix in the reaction of polymer-analogous transformations in order to obtain phosphorus-containing ICECAE 2024, 02035 (2024) E3S Web of Conferences https://doi.org/10.1051/e3sconf/202449702035 ICCEAE 2024.
The conditions for the phosphorylation of this polymer were selected from the experiments accumulated in relation to the phosphorylation reactions of low- and high-molecular compounds. The reaction scheme for obtaining a phosphate cation exchanger by phosphorylation of a styrene-furfural polymer with its subsequent oxidation in nitric acid can be represented as follows:

The resulting polymer had an exchange capacity for a 0.1 N NaOH solution – 5.5–5.6 meq/g and contained 16.5% phosphorus. In order to increase the exchange capacity, i.e. conversion of phosphine groups into phosphine, the polymer after washing with water was contacted for 7 hours at a temperature of 60°C with concentrated nitric acid. As a result, most of the phosphinic acid groups are oxidized to phosphinic acid groups. At the same time, the phosphorus content in the polymer does not change, the exchange capacity increases to 7.6–8.0 mEq/g. Table 1 shows the main properties of the phosphate cation exchanger obtained at different molar ratios of styrene to furfural.

From the data in Table 1 it can be seen that the phosphate cation exchanger with the best properties was obtained at a molar ratio of styrene to furfural of 1:1. Based on the studies carried out, the optimal conditions for the synthesis of the styrene-furfural polymer are assumed to be: the reaction temperature is 90°C, the concentration of the ZnCl₂ catalyst is 0.07 mol per mole of furfural, and the molar ratio of styrene to furfural is 1:1.

Table 1. Influence of the ratio of the starting materials on the properties of the resulting cation exchanger

<table>
<thead>
<tr>
<th>Molar ratio of styrene to furfural</th>
<th>Bulk weight, g/ml</th>
<th>Specific volume, ml/g</th>
<th>Static exchange capacity on, mEq/g</th>
<th>Mechanical strength, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2</td>
<td>0.68</td>
<td>2.2</td>
<td>5.6</td>
<td>0.8</td>
</tr>
<tr>
<td>1:1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

For phosphate cation exchangers, various types of metal bonds with ionogenic groups of the ion exchanger are characteristic: ionic bonds, mixed ion-coordination bonds and purely...
The type of bond is determined by the ability of a particular metal to form donor-acceptor complexes and the degree of dissociation of the ion exchanger. For metals capable of complexation, the formation of ion-coordination bonds with a uniform distribution of electron density over the four-membered cycle is possible. For this purpose, the interaction of the cation exchanger in Na- and H-forms with solutions of salts of copper sulfate, nickel, cobalt, sodium chloride, calcium, and uranyl nitrate were studied. The research results are shown in Table 2.

<table>
<thead>
<tr>
<th>0.1 N solutions</th>
<th>H-form</th>
<th>Na-form</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH solutions</td>
<td>Sorbed, mg-eq/g</td>
</tr>
<tr>
<td>CuSO₄₂·5H₂O</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>CuSO₄·5H₂O</td>
<td>2.64</td>
<td>2.7</td>
</tr>
<tr>
<td>CuSO₄·H₂O</td>
<td>2.1</td>
<td>2.0</td>
</tr>
<tr>
<td>NiSO₄·5H₂O</td>
<td>1.1</td>
<td>1.2</td>
</tr>
<tr>
<td>NiSO₄·H₂O</td>
<td>2.0</td>
<td>2.1</td>
</tr>
<tr>
<td>NiSO₄·H₂O</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>NiSO₄·H₂O</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>CoSO₄·H₂O</td>
<td>2.0</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Table 2. Sorption of metal cations by phosphate cation exchanger.

The data in Table 2 indicate the effect of the nature of the cation on the sorption capacity. It was found that the studied cations are sorbed by the cation exchanger differently and, according to their ability to sorption, can be arranged in the following order: Ni²⁺ > Cu²⁺ > Co²⁺ > Na⁺. In order to elucidate the mechanism of sorption of the cations of these metals, we took the IR spectra of the cation exchanger in the H and Na form, saturated with copper ions. According to the literature data, the vibration frequencies for phosphoric acid groups are in the range of 700-2560 cm⁻¹. In the spectrum of the cation exchanger in the H-form, bands are observed at 1150 cm⁻¹, corresponding to stretching vibrations of the phosphorus-oxygen bond. The absorption band at 1150 cm⁻¹ does not disappear in the spectrum of the cation exchanger in the Na-form.

The tested cation exchanger contains phosphoric acid groups differing in their acidic properties pK₁ = 2.8; pK₂ = 7.5. The less dissociated phosphoric acid groups, the stronger hydrogen bond forms phosphoryl oxygen with OH groups. Therefore, it can be expected that as the cation exchanger is saturated with sodium, the maximum of the band corresponding to the phosphorus-oxygen bond vibrations will slightly shift to longer wavelengths as a result of the destruction of the weaker hydrogen bond. In the spectrum of the cation exchanger in the H-form, there are not sharp broad bands in the range of 2600-2860 cm⁻¹, 2100-2600 cm⁻¹ related to the stretching vibrations of P-OH linked by hydrogen bonds. These bands disappear in the spectrum of the sodium-saturated cation exchanger. When considering the spectra of the cation exchanger saturated with metal ions, in contrast to the spectrum of the cation exchanger in the H-form, bands appear at 1060 cm⁻¹ for uranyl and 1055 cm⁻¹ for copper and nickel.

4 Conclusions

Phosphorylation of a styrene-furfural polymer has been used to obtain and investigate a phosphate cation exchanger characterized by high thermal-chemical resistance and...
Mechanical strength. The structure and properties of the obtained cation exchanger were studied using chemical methods of analysis in combination with IR spectroscopy, potentiometry, photocolorimetry, etc. It was shown that ions of copper, nickel, cobalt and uranyl ion are sorbed by phosphoric acid cation exchanger due to ion exchange and partly due to the formation of coordination bonds with an ionic group of a cation exchanger. The analysis of the data obtained indicates that the studied phosphate cation exchanger is sufficiently high for sorption ability to ions of the tested metals.

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