

Research Article

CuO-Loaded Macroreticular Anion Exchange Hybrid Polymers Obtained via Tetrachlorocuprate(II) Ionic Form

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Amberlite IRA900 Cl, the macroreticular, polystyrene/divinylbenzene anion exchanger containing quaternary ammonium groups, was used as the support for copper(II) oxide deposition, and, as a result a new hybrid ion exchanger (HIX) was obtained. The CuO deposit was introduced into the anion exchanger structure in two steps conducted batchwise at ambient temperature. First, the functional groups were transformed from the Cl^- into the CuCl_4^{2-} form, using 5 mol dm^{-3} NaCl or HCl solution with CuCl_2 being added, and then the intermediate product was contacted with NaOH/NaCl solution to precipitate CuO within the polymer beads. A HIX containing as much as 11.5% Cu was obtained. The distribution of the inorganic load within the porous matrix of polymer beads was atypical; CuO was mainly deposited in the outer parts of the beads and only a small amount was in their inner parts. This may be advantageous in some practical applications concerning the removal of harmful admixtures from waters in sorption processes.

1. Introduction

Hybrid ion exchangers (HIX) form a major group of hybrid polymers. They are obtained from synthetic ion exchangers into the structure of which an inorganic deposit is introduced. The presence of proper inorganic constituent results in excellent and selective adsorption properties of HIX for removal of target pollutants from contaminated water and wastewater, while same-sign functional groups of polymer matrix greatly enhance the permeation of the pollutant ion and its preconcentration prior to effective sorption by inorganic particles (the Donnan membrane effect) [1–3]. Due to their physical form (spherical beads), HIX can be used, as a bed in a column, in dynamic conditions. Amongst the metal oxides dispersed within the structure of ion exchangers, iron hydr(oxide)s are most commonly studied because of their affinity to many species such as heavy metal cations and harmful oxyanions, availability, and environmental friendliness [4, 5]. The knowledge relating to HIX keeps growing, covering new products and applications. However, only few

reports about synthesis of HIX containing CuO deposit have been published [6–8].

Copper(II) oxide is a chemical compound with various and unique properties which, due to the development of nanotechnology, finds increasingly wider application [9, 10]. These include, amongst others, use of CuO as promising nanostructured adsorbent for removal of undesirable and toxic contaminants such as As(III) and As(V), Pb(II), and Cr(VI) ions from water [11–19]. However, the use of CuO nanoparticles for water purification entails technical problems; particularly separation of the nanostructures from the treated water after the process is difficult. In practical situations, use of such adsorbents needs to be combined with another technique to prevent the release of the nanostructures into the purified water [20]. In order to exploit the good adsorption properties of CuO and limit the penetration of the cleaned water by the ultrafine particles, it is advisable to immobilize them within porous structure of a polymeric support. Simultaneously, the dispersion of this oxide within the matrix of the supporting polymer prevents agglomeration

of nanoparticles and ensures a large area of contact between the reagents in the sorption processes.

In our previous study, we have presented the synthesis of a new HIX containing CuO dispersed within the matrix of a strongly alkaline macroreticular anion exchanger (An) which was used as the polymeric support [8]. Our method of synthesis involved two steps: (a) ion exchange between An in the OH⁻ form and CuSO₄ solution aimed at obtaining an anion exchanger doped with Cu(OH)₂ particles and (b) the transformation of Cu(OH)₂ into CuO in NaOH solution at an elevated temperature. The final products contained up to 6.0% Cu.

In the work of other authors, a HIX containing CuO was obtained by a column method with the use of a microporous (gel-type) strongly alkaline anion exchanger whose functional groups were converted in the first step into tetrachlorocuprate(II) form [7]. The dispersion process brought the metal coverage of the internal bead surfaces to 4.8% Cu. Obtained sorbent containing hydrated CuO within its structure has been studied for phosphate removal from water. However, the ways of synthesis of this material and its characterization were not reported in detail.

The aim of this study was to optimize the CuO content in the anion exchanger macroreticular structure and to analyze the distribution of the deposit within the beads. They are major factors affecting the HIX's sorption capacity and the sorption and desorption kinetics in water purification processes. Since medium conditions under which the functional groups of the anion exchanger transformed from the Cl⁻ to the CuCl₄²⁻ form have not yet been studied, it is worthwhile to determine the reaction medium composition which ensures quantitative ion exchange reaction. This is a prerequisite for a high CuO content in the end product obtained after alkalization of the reaction medium. In this study we wanted to answer the following questions: (a) in what conditions does the quantitative transformation of the functional groups of the anion exchanger into the form CuCl₄²⁻ occur? (b) What portion of the copper bonded by the functional groups remains in the ion exchanger phase after the alkalization of the reaction medium? (c) How are the CuO particles distributed within the polymer beads considering that in the alkaline medium the anion-exchangeable functional groups of the anion exchanger repel Cu²⁺ ions since both reagents have the same charge?

2. Materials and Methods

All the chemicals used in this study were of analytical grade. All the solutions were prepared using deionized water. Amberlite IRA900 Cl (Dow Chemical Co.), a macroreticular, polystyrene/divinylbenzene strongly alkaline anion exchange resin containing quaternary ammonium groups (amounting to 3.18 meq/g of the dry resin), was selected as the macromolecular host material for the CuO deposit.

The anion exchanger in the Cl⁻ form (An/Cl⁻) was dried at 40°C for 24 h. An An/Cl⁻ sample weighing about 1.0 g (3.18 meq) was placed in a conical flask and treated with 10 cm³ of 0.5 mol dm⁻³ CuCl₂ in HCl solution with a concentration of 2–6 mol dm⁻³ and in NaCl solution with

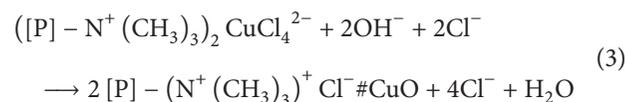
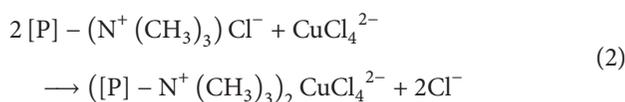
a concentration from 2 mol dm⁻³ (pH 2.97) to 5 mol dm⁻³ (pH 2.50). The reagents were shaken at 20°C for 1 h. The filtered-off intermediate product was introduced into 1 mol dm⁻³ NaOH in 1 mol dm⁻³ NaCl solution (50 cm³) and was shaken at 20°C for 24 h. After the reaction, the sediment was removed through decantation and the filtered-off and washed product was dried at 40°C for 24 h.

The Cu content in the products was determined after dissolving CuO in acid solution. A sample weighing about 0.5 g was treated with 10 cm³ of 2 mol dm⁻³ HCl in a conical flask and shaken for 30 min. After this time, the polymer beads were filtered off into a volumetric flask having a volume of 50 cm³. Then 10 cm³ of the solution was drawn; the sample was alkalized with concentrated aqua ammonia and titrated with 0.05 mol dm⁻³ EDTA against murexide. Analyses were performed duplicate with standard deviation not exceeding 1.0%.

Microscopic examinations were performed by means of a HITACHI S-3400N scanning electron microscope (SEM) equipped with an energy-dispersive spectrometry (EDS) microanalyzer. Specific surface area and the porous characteristics were determined from the adsorption isotherms for liquid nitrogen at 77 K using an Accelerated Surface Area and Porosimetry Analyzer (ASAP 2020, 2007, Micromeritics). The crystalline structure was determined using the X-ray diffraction technique (ULTIMA IV/Rigaku).

3. Results and Discussion

It is not easy to dope CuO particles within the matrix of anion exchanger because the precursor of such particles, that is, Cu²⁺ ions, cannot be ion exchanged onto an anion exchanger. Considering that there exists a copper containing anion, that is, CuCl₄²⁻, we decided to exploit it as the precursor of CuO with the affinity toward strongly alkaline anion exchanger. Proper concentrations of HCl and NaCl solutions, ensuring the quantitative transformation of the anion exchanger functional groups from the Cl⁻ form into the CuCl₄²⁻ form and then proper conditions for transforming the intermediate product in such a way that as much as possible of the CuO remained in the ion exchanger phase, were sought:



where [P] is the polymer matrix (macroreticular styrene-divinylbenzene copolymer) and # stands for deposited within polymer matrix.

Since CuCl₄²⁻ ion forms exclusively in media with a high Cl⁻ ion content, two series of concentrated NaCl and HCl solutions were prepared and a precursor, that is, CuCl₂, was introduced into them. When the solutions turned green,

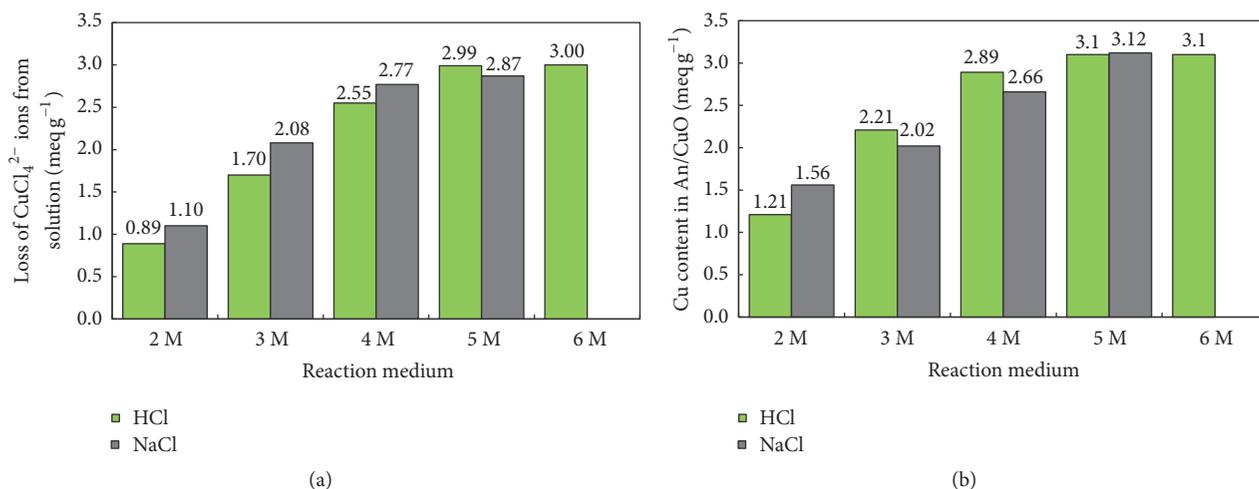


FIGURE 1: (a) Loss of CuCl_4^{2-} ions from the solutions in batch reaction at ambient temperature (1.0 g An/Cl^- in 10 cm^3 of $0.5 \text{ mol dm}^{-3} \text{ CuCl}_2$ in different media) and (b) Cu content in corresponded HIX.

this indicated that CuCl_4^{2-} ions had formed. The solutions ($10 \text{ meq CuCl}_4^{2-}$) were shaken with anion exchanger samples (3.18 meq). After a few minutes, the cream-coloured anion exchanger beads turned intensively yellow. After 1 h, the beads were separated and the solutions were analyzed for copper content. Figure 1(a) shows that the loss increased with the increase in the concentration of the NaCl and HCl solutions (no results for 6 mol dm^{-3} NaCl are shown due to the limited solubility of this salt in water). In the solutions with the highest concentrations, the copper loss reached 3.0 meq and it was close to the anion exchanger's capacity, which indicated that the transformation of the functional groups into the CuCl_4^{2-} form was almost quantitative, consistently with reaction (2). The reaction medium (HCl or NaCl) was found to have no significant effect on the course of reaction (2). It was found that the reaction was accompanied by a decrease in pH: the initial pH of $0.5 \text{ mol dm}^{-3} \text{ CuCl}_2$ in 5 mol dm^{-3} NaCl was 2.50 and after the reaction it amounted to 2.35.

The ion exchanger samples were transferred onto filter papers in order to separate as much as possible the reaction medium from them. They could not be washed with deionized water since this would immediately result in the release of copper from the functional groups (the decrease in Cl^- concentration causes the decomposition of CuCl_4^{2-} ion). Therefore, the moist samples were introduced into the NaOH/NaCl solution (NaOH caused precipitation of CuO while NaCl caused transformation of the ion exchanger functional groups into the Cl^- form). In the course of 24 h long shaking, the ion exchangers changed their colour from yellow to blue (in a few minutes) and then to black (in a few hours). The water phase contained a small amount of black deposit. The HIX samples taken from the 5 mol dm^{-3} HCl and 5 mol dm^{-3} NaCl media contained the largest amount of copper, that is, over $3.1 \text{ meq Cu g}^{-1}$ (Figure 1(b)). Interestingly, almost all the HIX samples contained markedly more copper than the amount of copper lost from the solutions after the first step. This indicated that some of the CuO depositing in the ion exchanger came from the decomposition of the free

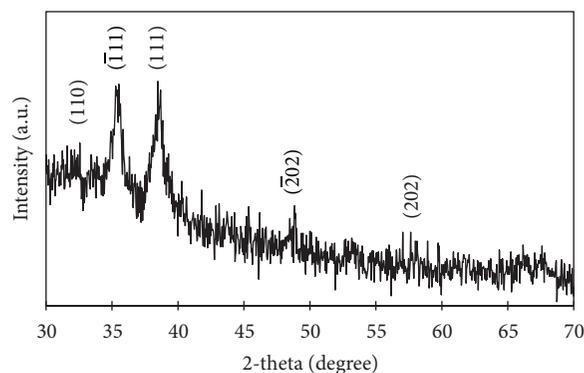


FIGURE 2: X-ray diffraction pattern of the obtained hybrid polymer.

CuCl_4^{2-} ions contained in the water phase remaining in the porous structure of the polymer beads after filtration.

Further research focused on modifying the filtering of the ion exchanger after the first step. Samples taken from the 5 mol dm^{-3} NaCl and 5 mol dm^{-3} HCl media were used for this purpose. Gravitational filtration was replaced with vacuum filtration (a Büchner funnel). The aim of modifying the filtering technique was to more precisely separate the postreaction medium from the ion exchanger. It was found that the vacuum-filtered products subjected to the reaction with NaOH/NaCl contained more copper (even to $3.5 \text{ meq Cu g}^{-1}$) than the gravitationally filtered products. This may be due to lower moisture content in the ion exchanger sample after vacuum filtering, whereby the reagent (NaOH/NaCl solution) can penetrate faster into the ion exchanger beads.

The chemical composition of the inorganic deposit introduced into supporting, polymeric material was determined by X-ray diffraction (XRD).

The XRD pattern, presented in Figure 2, revealed that the inorganic load in the final product consisted mainly of copper(II) oxide, CuO. The relatively broad reflections at

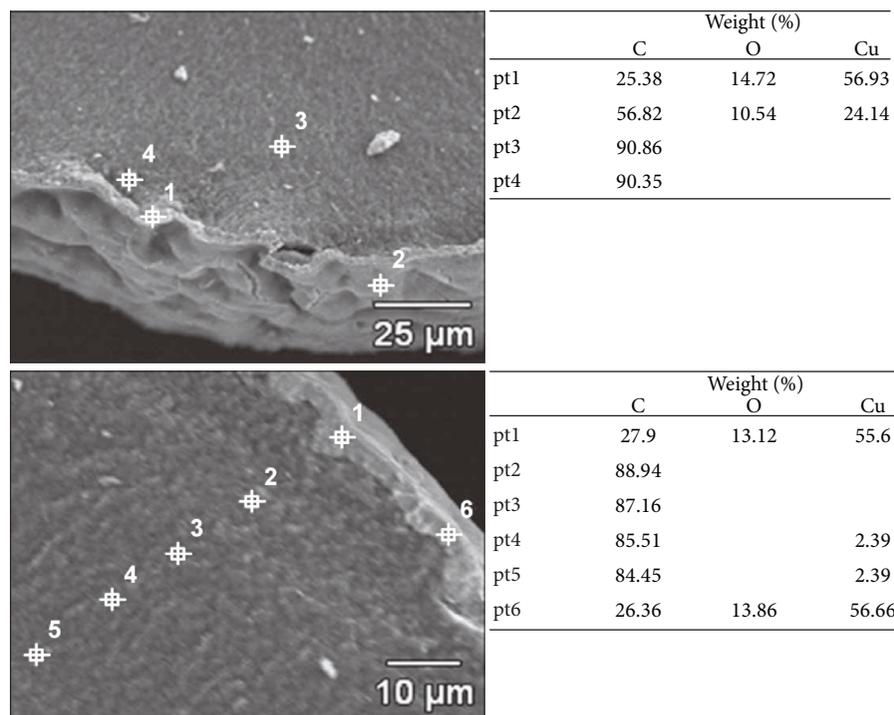


FIGURE 3: SEM image with EDS analysis of the cross section of the polymer bead impregnated with CuO.

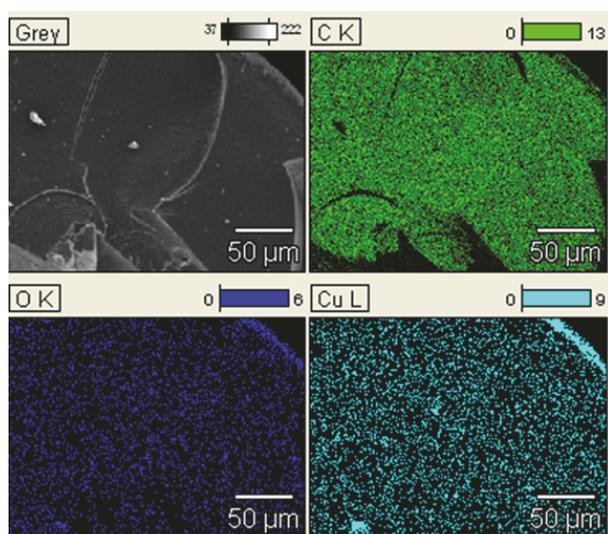


FIGURE 4: SEM image with EDS mapping analysis of distribution of copper, carbon, and oxygen on the cross section of the polymer bead impregnated with CuO.

2θ : 32.5°, 35.5°, 38.5°, 48.5°, and 58.3° were matched with ICSD card number 87126. The dispersion of inorganic deposit within the polymer matrix was analyzed using the SEM EDS technique (Figures 3 and 4).

The obtained results show that the precipitated copper(II) oxide was dispersed mainly in the outer parts of the polymeric beads, while their inner parts contained only a very small

amount of evenly scattered CuO (Figures 3 and 4). This may be explained by the course of the copper(II) oxide deposition within the porous structure of the ion exchanger's beads. This process consisted of four main stages: (a) introduction of CuCl_4^{2-} ions into the functional groups, (b) decomposition of tetrachlorocuprate(II) after alkalization, (c) precipitation of $\text{Cu}(\text{OH})_2$, and (d) conversion of $\text{Cu}(\text{OH})_2$ to CuO. As mentioned earlier, the transformation of the functional groups into the CuCl_4^{2-} form was almost quantitative, ensuring uniform dispersion of Cu within the polymer beads. As a result of decomposition of tetrachlorocuprate(II), the Cu^{2+} ions were temporarily formed and diffused from the inner to the outer part of the beads due to electrostatic repulsion. This process was favoured by the presence of macropores within the polymeric structure of the ion exchangers. The contact of highly alkaline bulk solution with the surface of the polymeric bead resulted in immediate precipitation of $\text{Cu}(\text{OH})_2$ in the outermost part of the beads. This layer, formed at the first stage of the precipitation process, then acted as a barrier to Cu^{2+} ions diffused from the bulk phase of the polymer. Precipitated copper(II) hydroxide was then converted into CuO within a few hours, which resulted in the colour of the beads changing from blue to black. The mechanism of this conversion is reconstructive, involving $\text{Cu}(\text{OH})_2$ dissolution followed by CuO precipitation [21]. The determined specific surface area (Table 1), typical for nonporous materials, confirmed the creation of an almost impermeable layer of copper(II) oxide in the outer part of the polymer beads.

It should also be noted that the presence of the copper in the whole cross section of the beads (Figure 4) and

TABLE I: Porous characteristics of the obtained hybrid polymer.

| $S_{\text{BET}}, \text{m}^2 \text{g}^{-1}$ | V_T (pore volumes), $\text{cm}^3 \text{g}^{-1}$ | L_m (mean pore diameter), nm |
|--|--|-----------------------------------|
| 2.88 | 0.0069 | 9.54 |

simultaneously the lack of CuO microdimensional aggregates (Figure 3) may suggest the formation of nanoparticles. Likewise, the broadening of XRD reflections (Figure 2) indicates that the precipitated particles of CuO are nanodimensional.

4. Conclusions

The obtained hybrid anion exchanger contained considerably more CuO than the similar products described earlier. The synthesis was conducted in a simple way, that is, batchwise at ambient temperature, without organic solvents. The product contained more deposit compared to that would be expected from the anion exchanger's functional groups content, since CuO formed not only from the CuCl_4^{2-} ions bound with the ion exchanger but also from the free CuCl_4^{2-} ions derived from the water phase remaining in the polymer beads after vacuum filtration. The specific distribution of copper(II) oxide within the porous polymer structure, "impregnation" of the outer parts of the beads and only a small amount of copper(II) oxide in their inner parts, may be advantageous in some practical applications. In adsorption processes, due to the high content of copper(II) oxide readily available in the outer part of the sorbent beads, a high process kinetic rate may be achieved as well as high regeneration efficiency. However, detailed research needs to be conducted on adsorption properties of the obtained product including equilibrium, kinetics, and column studies.

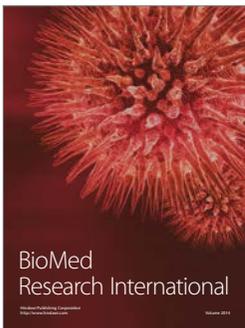
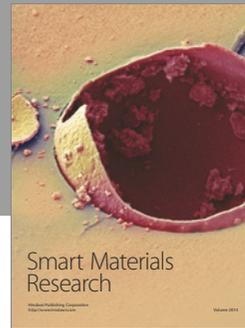
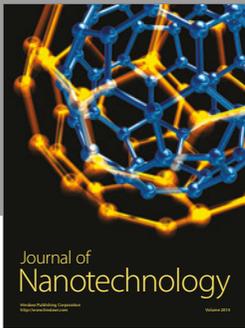
Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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