



Synthesis and characterization of CuO-loaded macroreticular anion exchange hybrid polymer



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ABSTRACT

The aim of this work was the study on the synthesis of hybrid polymers containing cupric hydroxide and oxide using as the supporting material macroreticular strong base anion exchanger. The first step of inorganic deposit introduction within the polymer matrix was precipitation of $\text{Cu}(\text{OH})_2$ under different conditions ($\text{Cu}(\text{II})$ salt, temperature, duration). This stable product containing even $60 \text{ mg Cu}(\text{II}) \text{ g}^{-1}$ was obtained by contacting anion exchanger in the OH^- form with CuSO_4 solution. In the second step $\text{Cu}(\text{OH})_2$ deposited in the polymer structure was converted into CuO under different conditions of which treatment with alkaline solution at a temperature of 50°C occurred with the highest efficiency. Hybrid polymers with CuO deposit after two-steps synthesis contained $54 \text{ mg Cu}(\text{II}) \text{ g}^{-1}$. Simultaneously, by repeating the synthesis cycle twice it was possible to increase $\text{Cu}(\text{II})$ load to 119 mg g^{-1} . The presence of cupric oxide was confirmed by XRD diffraction and FTIR analyses. SEM analyses showed that deposition of inorganic load occurred within the polymer matrix but in the outer parts of anion exchanger beads. Simultaneously, both obtained products containing $\text{Cu}(\text{OH})_2$ and CuO had almost the same porous characteristics in comparison to host polymer (determined BET surface area reached values: $20.71, 21.04, 18.90 \text{ m}^2 \text{ g}^{-1}$ respectively).

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1. Introduction

Hybrid polymers are organic macromolecular compounds containing an inorganic deposit, e.g. metal oxides. These materials have specific physical and chemical properties resulting from the synergy between the two components [1,2]. The dispersion of the inorganic component in the structure of synthetic ion exchangers is one of the possible ways of obtaining hybrid polymers. In this case the organic ion (cation or anion) exchanger plays the role of a water-swelling porous carrier for the metal oxide deposit. The dispersion of the metal oxides in the matrix of the supporting polymer, having a large specific surface area, prevents particle agglomeration and ensures a large area of contact between the reagents in the processes of catalysis and sorption. Moreover, due to its suitable physical form (spherical beads) the material can be used in dynamic conditions in fixed bed column systems. Such materials are usually obtained in several steps – first the functional groups of the cation or anion exchanger are transformed into a proper ionic form, followed by inorganic deposit precipitation in the structure of the polymeric beads using solutions of various precipitating agents. The obtained products still contain anion- or cation-exchange functional groups endowing them with characteristic properties. When the products are

used in sorption processes, the presence of anion exchange groups favours the removal of anionic impurities from waters, while the presence of cation exchange groups favours the removal of cationic impurities from water. Considering the potential use of the synthesized materials, the fact that ion exchange groups in an organic carrier can both promote and hinder (due to the Donnan exclusion effect) sorption processes is taken into account [3–5]. Because of their affinity to many species, low cost, easiness to obtain and environmental friendliness, iron oxide and hydroxides are the most studied inorganic constituents of hybrid ion exchangers. At present first ion exchangers containing CuO has been also obtained [6,7].

CuO is one of the most studied p-type semiconductor oxides. Its nanostructures arouse much interest since they have unique physicochemical properties and offer good development prospects as regards new applications. The relevant issues were presented in a recently published review [8]. A new application of CuO nanoparticles (CuO -NPs) is water purification and, more precisely, the removal of undesirable components from water through sorption [9,10]. Most studies on the subject deal with arsenic removal [11–16], and only a few papers are devoted to the removal of hydrogen sulphide [17] and heavy metals (Pb^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+}) [18].

So far the sorptive properties of CuO -NPs have been studied mainly from the point of view of their suitability for removing inorganic forms of arsenic, such as $\text{As}(\text{V})$ and $\text{As}(\text{III})$, from waters. K.J. Reddy and his team [11–14] initiated research on this subject. Arsenic species, highly harmful to the human body, occur in elevated concentrations in natural

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waters which are sources of drinking water for the inhabitants of many regions of the world, practically on all the continents. One of the major global environmental challenges is to provide millions of people with potable water with an arsenic concentration below $10 \mu\text{g As dm}^{-3}$. In order to reduce the elevated levels of arsenic in water, various sorbents, including metal oxides, have been extensively investigated [19–21]. Recently CuO-NPs have been found to be promising arsenic adsorbents which circumvent many of the obstacles other treatment techniques may encounter. In sorption processes CuO-NPs show many advantages, such as a high As adsorption capacity, an ability to adsorb arsenic under natural conditions (in the presence of competing anions without adjusting the pH or oxidation state of arsenic, since CuO-NPs are able to adsorb both arsenate and arsenite) and an ability to regenerate by leaching with a NaOH solution, owing to which the spent adsorbent can be reused.

For sorption purposes nanometre-sized CuO particles were obtained by refluxing an ethanolic solution of CuCl_2 and NaOH. After the reaction the dark brown precipitate was centrifuged and washed with hot deionized water, ethanol and acetone. Finally, the product was dried at room temperature and heated to 110°C [11,13]. Larger, micrometre-sized CuO particles ($\leq 5 \mu\text{m}$ in diameter) were obtained by reacting at room temperature a water solution containing the same reagents (CuCl_2 and NaOH). CuO microparticles (CuO-MPs) were separated by filtering through a paper filter and then washed with deionized water and dried at $250\text{--}300^\circ\text{C}$ [12]. Three-dimensional (3D) hierarchical cotton candy like CuO nanostructures were prepared by the solvothermal method using $\text{Cu}(\text{CH}_3\text{COO})_2$ and urea in ethylene glycol and by the subsequent calcination of the precursor at 400°C [16].

CuO-NPs as arsenic sorbents were mainly used in batch equilibrium experiments [11–13,15,16]. The experiments were conducted using a wide variety of collected groundwater samples (from the western US and from West Bengal, India), different process parameters, and the CuO-NPs concentration of $0.2\text{--}10 \text{ g CuO dm}^{-3}$. Also continuous flow-through experiments were conducted to extend the studies and to develop a one-step process for removing arsenic from natural groundwater [14]. The flow-through column consisted of two compartments. Water would be fed into the lower compartment and mixed with CuO-NPs slurry by means of a magnetic stirrer to remove arsenic. The treated water would be received in the upper compartment and CuO-NPs would be retained on a sand filter. A micro-glass filter (with the pore size of $4\text{--}8 \mu\text{m}$) situated above the sand layer was used to capture any CuO-NPs escaping from the sand.

The use of CuO-NPs to remove arsenic from waters brings several advantages, but also technical problems, and potential hazards arise. It is difficult to remove CuO-NPs from the spent solutions in order to, e.g., determine their composition. After the reactions, before being analysed, the solutions were centrifuged for a few minutes (to allow CuO-NPs to settle at the bottom of the tubes) and then the supernatant was filtered with a $0.45 \mu\text{m}$ membrane or syringe filter [11,13,15,16]. This means that in the case of larger-scale water purification the problem of the efficient separation of CuO-NPs will need to be solved. It is also necessary to determine the Cu concentrations in the water after treatment with CuO-NPs. By comparing the chemistry of groundwater samples before and after the process it was found that the use of CuO-NPs resulted in an increase in the copper concentration in the treated samples, which was evidence of the release of copper into the water environment. The copper concentration in the groundwater samples would increase to different degrees. In one case it increased from 10 to as much as $980 \mu\text{g Cu dm}^{-3}$. However, the Cu concentrations in both the treated and untreated samples were in each case below the US EPA MCL of $1300 \mu\text{g Cu dm}^{-3}$ [12]. The toxicity of Cu-based NPs (Cu^0 -NPs, CuO-NPs) and soluble Cu(II) ions towards different trophic groups involved in anaerobic and anoxic wastewater treatment processes has been intensively studied recently. It has been shown that extended exposure to CuO-NPs reduces acetoclastic methanogenic activity by over 85%. It has also been shown that CuO-NPs undergo

multidirectional chemical transformations in biological and environmental media. The bioavailability, redox activity and toxicity of such particles are investigated since the transformations are relevant to living systems [22–24].

In the studies dealing with the removal of arsenic in batch conditions it is noted that the use of nanoadsorbents needs to be combined with other conventional techniques in practical situations to prevent the release of CuO nanostructures into the cleaned water [16]. In one study [25] activated mesoporous alumina characterized by a high surface area, impregnated with CuO, was used to remove arsenic from water in batch adsorption processes. The mesoporous alumina containing CuO was prepared by treating activated alumina with a CuSO_4 solution, raising the pH to 4.5–5.0 by adding 0.1 M NaOH and then calcinating the solid residue at 450°C . The paper does not specify the copper content in the adsorbent. However, it is stated that this modification significantly improved the adsorption of arsenic (from 0.92 to 2.16 mg g^{-1} for As(III) and from 0.84 to 2.02 mg g^{-1} for As(V)) and that there was no leaching of copper during the treatment.

In order to exploit the good adsorption properties of CuO and limit the penetration of CuO-NPs into the cleaned water, the present authors undertook an attempt to incorporate CuO into the matrix of ion exchange resins. Hybrid polymer containing a CuO deposit, obtained from an anion exchanger could be an effective sorbent in the processes of removing anionic impurities from waters. Recently, novel selective hybrid cation exchanger and anion exchanger containing cupric oxide were obtained for removal from water ammonia nitrogen and phosphate respectively [6,7]. However, the synthesis method of these materials and their characterization was not studied in detail. The aim of this study was to obtain a hybrid polymer containing a CuO deposit, using a strongly alkaline macroreticular anion exchanger, through the following transformations:

where:



An/Cl anion exchange resin in the Cl^- form,
 An/OH anion exchange resin in the OH^- form,
 An/ SO_4 anion exchange resin in the SO_4^{2-} form,
 An/ $\text{SO}_4\#\text{Cu}(\text{OH})_2$ anion exchange resin in the SO_4^{2-} form with $\text{Cu}(\text{OH})_2$ in the polymer matrix (simply put: An/ $\text{Cu}(\text{OH})_2$) where # stands for deposited within polymer matrix,
 An/ $\text{SO}_4\#\text{CuO}$ anion exchange resin in the SO_4^{2-} form with CuO in the polymer matrix (simply put: An/ CuO) where # stands for deposited within polymer matrix,
 and subsequently to determine the amount and distribution of the inorganic deposit in the beads and the effect of this deposit on the characteristics of the surface of the new material (in comparison with the parameters determined for the initial polymeric feedstock).

2. Material and methods

2.1. Materials

The polymer support for CuO was Amberlite IRA 900Cl – the commercial anion exchange resin produced by The Dow Chemical Co. All the chemicals used in this study, including $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, CuCl_2 (PPH Stanlab, Lublin, Poland) ammonia solution 25%, NaOH, H_2SO_4 96%, NaOH fix, EDTA fix, and murexide (Chempur, Piekary Śląskie, Poland), were of analytical grade. All the solutions were prepared using deionized water.

In order to transform the anion exchanger functional groups into the OH^- form, 1 M NaOH and subsequently deionized water were passed

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