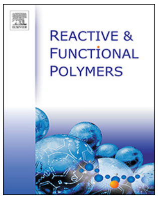
Reactive and Functional Polymers 127 (2018) 129–138

Contents lists available at ScienceDirect

Reactive and Functional Polymers

journal homepage: www.elsevier.com/locate/react



Hybrid ion exchangers containing Fe(III)-Cu(II) binary oxides obtained using macroreticular anion exchanger

Elżbieta Kociołek-Balawejder[a,*], Ewa Stanisławska[a], Katarzyna Winiarska[b], Juliusz Winiarski[c], Mariusz Hasiak[d], Bogdan Szczygieł[c], Irena Szczygieł[b]

[a] *Department of Industrial Chemistry, Wrocław University of Economics, Komandorska 118/120, 53-345 Wrocław, Poland*
[b] *Department of Inorganic Chemistry, Wrocław University of Economics, Komandorska 118/120, 53-345 Wrocław, Poland*
[c] *Department of Advanced Material Technologies, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*
[d] *Department of Mechanics, Materials Science and Engineering, Wrocław Univeristy of Science and Technology, Smoluchowskiego 25, 50-370 Wrocław, Poland*

ARTICLE INFO

Keywords:
Anion exchanger
Hybrid ion exchanger
Fe-Cu binary oxides
Copper ferrite
Tetrachloroferrate ion
Tetrachlorocuprate ion

ABSTRACT

Considering the performance of parent Fe(III)-Cu(II) binary oxide nanoparticles in removing numerous contaminants from water, in order to prevent the release of the nanostructures into the cleaned water a deposit with the same composition was introduced into the matrix of a synthetic porous material (ion exchange resin), whereby a hybrid ion exchanger (HIX) was obtained. Amberlite 900 Cl, a commercially available strongly basic macroreticular anion exchanger, was used as the supporting material. The inorganic deposit was introduced into its structure in two steps performed batchwise at ambient temperature. Fe(III)-Cu(II) binary oxide could be deposited into the matrix of the strongly basic anion exchanger owing to the affinity of its functional groups for $FeCl_4^-$ and $CuCl_4^{2-}$ ions. When in the ion exchange reaction the anion exchanger bound both the ions and the reaction medium alkalized, the respective oxides FeOOH and CuO precipitated in its structure. The oxide deposit was introduced into the ion exchanger in three ways, whereby HIXs differing in their oxide content, in the mole ratio of the oxides and in the latter's atypical distribution in the matrix of the anion exchanger were obtained. Regardless of the method of conducting the reaction, HIXs rich in oxides, e.g. 3.73 mmol (Fe, Cu) g^{-1} (2.35 mmol Fe and 1.38 mmol Cu g^{-1} at Fe/Cu = 1.7) were obtained. The products were investigated by SEM, EDXS, T/TG/DTA, XRD and VSM. The doped HIXs are characterized by a core-shell structure, where the core consists of polymeric beads and the outer thin layer contains Fe and Cu in their oxidized form. The structure of the outer layer varies depending on the procedure of precipitation. These differences are also reflected in the magnetic properties (ferromagnetic or paramagnetic interaction). $CuFe_2O_4$ was found to be present in the samples sintered at 900 and 1300°C, which proves that a ferrite can form from the deposit after a solid-state reaction at high temperatures.

1. Introduction

Numerous contaminants, some of which have serious side effects and toxicities, with a few being lethal and cancerogenic, occur in many regions of the world (including Europe) in waters of different type and origin, including in natural waters abstracted for public water supplies. The most dangerous inorganic water pollutants are arsenite/arsenate (arsenic tops the Priority List of Hazardous Substances Agency for Toxic Substances and Disease Registry, Atlanta, USA) and, heavy metals such as lead, mercury, cadmium and chromium [1,2]. Therefore a major global challenge today is to provide clean and safe drinking water for humans. Great efforts have been made to develop effective and affordable technologies for removing pollutants from water. Adsorption ranks high among the various technologies employed for water treatment [3,4]. At present it is by far the most investigated water treatment process, offering many advantages, such as the availability of a wide range of adsorbents, operational simplicity and cost effectiveness. The development of nanotechnologies in the last two decades, resulting in highly effective novel materials, has contributed to the popularity of adsorption in water treatment methods [5]. Porous nanosize particles (NPs) and nanocomposites with a large surface area, a high sorption capacity and high reactivity have made it possible to effectively isolate noxious impurities from polluted water [6]. Owing to their unique physical and chemical properties, several metal oxide/oxyhydroxide/hydroxide nanostructures containing Fe, Ti, and Mn are the most relevant adsorbents under study. Iron oxides and oxyhydroxides as well as

---

* Corresponding author.
E-mail address: elzbieta.kociolek-balawejder@ue.wroc.pl (E. Kociołek-Balawejder).

https://doi.org/10.1016/j.reactfunctpolym.2018.04.009
Received 8 January 2018; Received in revised form 27 March 2018; Accepted 16 April 2018

zero-valent iron, advantageously characterized by nontoxicity, chemical inertness, biocompatibility and ease of preparation, are reported as efficient sorbents of many water and wastewater contaminants [7,8]. For several years now CuO NPs have been used in sorption processes to remove arsenic species from waters. As arsenic species sorbents, CuO NPs have many advantages: the pH of the cleaned water need not be adjusted, there is no need to oxidize As(III) to As(V) and the presence of the competing anion in the water being treated only slightly disturbs the process [9–16]. Moreover, different CuO nanostructures have been employed in removing Pb(II) [17,18] and Cr(VI) ions from waters [19,20].

Attempting to obtain sorbents with improved adsorption properties researchers replaced single metal oxides with mixed bimetal oxides (binary oxides). When developing composite sorbents containing two or more metal oxides they found that the composite not only inherited the advantages of the parent oxides, but also showed a synergistic effect. For example, a nanostructured binary Fe(III)-Cu(II) oxide with a molar Fe/Cu ratio of 2:1 showed excellent performance in removing arsenic species from water and its maximal adsorption capacities for As(V) and As(III) at pH 7.0 were as high as 82.7 and 122.3 mg g^{-1} respectively [21]. It was found that the combination of a copper(II) oxide with an iron(III) oxide resulted in a significant improvement in arsenic sorption in comparison with the use of one of the oxides and that the molar Fe/Cu ratio was a key factor influencing the sorption capacity of the binary oxides. A similarly obtained series of Cu-Fe binary oxides was used to remove phosphate from water [22]. Again, the adsorbent with a molar Fe/Cu ratio of 2:1 showed the highest phosphate adsorption capacity of 35.2 mg g^{-1} at pH 7.0 (pure CuO had a very low phosphate capacity of 3.9 mg g^{-1} while the adsorption capacity of phosphate on pure FeOOH amounted to 12.6 mg g^{-1}). This indicated that the addition of the Cu(II) oxide to the Fe(III) oxide had substantially improved the phosphate adsorption capacity. In [23] a binary Fe-Cu oxide was prepared and used to remove hexavalent chromium from an aqueous solution at pH 3–9. Binary Fe-Cu oxides with different molar ratios were synthesized and their performance in removing antimony from an aqueous solution was evaluated. A comparative test indicated that the molar Fe/Cu ratio of the prepared binary oxides greatly influenced Sb(III) removal and the optimum molar Fe/Cu ratio was about 3:1 [24]. The maximum adsorption capacity of 209.23 mg g^{-1} at the pH of 5.0 was achieved. The same molar ratio of the oxides (3:1) in the adsorbent was found to be most advantageous for removing Sb(V) from water [25]. The maximum adsorption capacity of 191.9 mg g^{-1} at the pH of 6.0 was higher than that of many other adsorbents.

Generally, parent oxide NPs (both single and mixed) are extremely effective reagents for water treatment in batch processes. Most of them are synthesized as a suspension in an aqueous solution and are available in the form of fine powders, which are unsuitable for column applications, which is a limitation in comparison with conventional adsorbents such as active carbon. There are also other limitations to the use of NPs. The separation and recovery (by magnetic separation, cross-flow membrane filtration and centrifugation) of NPs after the process is both difficult and expensive. Since NPs are extremely small they can penetrate in an uncontrolled way into all the spheres of the natural environment (and ultimately into the human body) during their application and disposal, which can have hard-to-predict consequences. The problems stemming from the toxicity of NPs and their long-term impact on nature have not been sufficiently explored yet, though the research in this field is very intensive [26,27].

In order to make practical water treatment processes more efficient, exploit the good adsorption properties of metallic oxide NPs and prevent the release of nanostructures into the cleaned water, it is worthwhile to introduce NPs into the matrix of such synthetic porous materials as ion exchange resins to obtain hybrid ion exchangers (HIXs). Several studies have shown that HIXs combine the advantageous sorption properties of inorganic particles with the excellent hydraulic characteristics of ion exchangers. The dispersion of metallic oxides into the matrix of the supporting polymer prevents the agglomeration of ultrafine particles and ensures a large area of contact between the reagents in the sorption processes. Moreover, thanks to the suitable physical form of HIXs (spherical beads) they can be used (instead of parent NPs) in dynamic conditions in fixed bed column systems. The functional groups of HIXs can facilitate the sorption of a particular water constituent. For example, the presence of electropositive functional groups in an anion exchanger-based HIX favors the migration of the anions present in water deep into the polymeric phase, enabling their sorption onto NPs (the Donnan membrane effect) [28–30].

The aim of the present research was to incorporate binary Fe-Cu oxides into the matrix of a strongly basic macroreticular anion exchanger. So far a HIX that is an anion exchanger with such a deposit has not been reported. We selected this ion exchanger as the oxide phase carrier considering that: (1) the above-mentioned contaminants removed by mixed Fe-Cu parent oxides were anions and that consistently with the Donnan membrane effect the electropositive groups of an anion exchanger should aid the sorption of such water contaminants and (2) owing to the ion exchanger's macroporous structure large-sized ions ($FeCl_4^-$ and $CuCl_4^{2-}$) used as the substrates could move freely in the resin into the center of a bead.

We have presented the synthesis of two HIXs based on the same anion exchanger, which contained a single oxide CuO [31] or FeOOH [32]. The inorganic deposit was introduced into the anion exchanger in two steps conducted batchwise. First, the functional groups were quantitatively transformed from the Cl^- into the $CuCl_4^{2-}$ or $FeCl_4^-$ form, then the intermediate product was contacted with NaOH solution to precipitate cupric oxide or hydrate ferric oxide into the grains. Attempting now to introduce a binary oxide made up of these oxides (CuO and FeOOH) into a polymeric carrier it should be noted that these oxides may be a “precursor” of copper ferrite $CuFe_2O_4$ – a compound which shows both adsorption and magnetic properties. A HIX containing such a deposit could be separated from water by a magnet. Currently, spinel ferrite magnetic NPs are considered as alternative future materials for water purification (adsorbents of toxic metal ions and dye molecules) [33]. Their deposition into the matrix of a porous carrier represents an important step in the development of such materials as HIXs.

2. Materials and methods

2.1. Materials

The polymer support for Cu(II)-Fe(III) binary oxide was Amberlite IRA 900 Cl, the commercial anion exchange resin produced by The Dow Chemical Co. All the chemicals used in this study, including $FeCl_3{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, ammonia solution 25%, ethyl alcohol 99.8%, murexide, analytical weighed amount of ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) (Chempur, Piekary Śląskie, Poland), NaOH, HCl 35–38%, NaCl (PPH Stanlab, Lublin, Poland), and salicylic acid (POCh, Gliwice, Poland) were of analytical grade. All the solutions were prepared using deionized water.

2.2. Preparation of the hybrid polymers

The anion exchanger in the Cl^- form (An/Cl^-) was dried in a chamber dryer at 40 °C for 24 h. An An/Cl^- sample weighing about 1.0 g was placed in a conical flask and treated with one of the solutions: 0.5 mol dm^{-3} $FeCl_3$ in 5 mol dm^{-3} HCl (in short: the Fe/HCl solution), 0.5 mol dm^{-3} $CuCl_2$ in 5 mol dm^{-3} HCl (in short: the Cu/HCl solution), 0.5 mol dm^{-3} $CuCl_2$ in 5 mol dm^{-3} NaCl (in short: the Cu/NaCl solution) or a mixture of the Fe/HCl and Cu/HCl solutions (Table 1). The reagents were shaken at 20 °C for 1 h. Then, the vacuum filtered off intermediate product was introduced into 50 cm^3 of 1 mol dm^{-3} NaOH in 1 mol dm^{-3} NaCl (in short: the NaOH solution) and was shaken at 20 °C for 24 h. The inorganic sediment was removed through