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Research Paper

Iron(III) (hydr)oxide loaded anion exchange hybrid polymers obtained via tetrachloroferrate ionic form—Synthesis optimization and characterization

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ABSTRACT

This study focused on the synthesis optimization and characterization of hybrid ion exchangers (HIX) containing iron(III) (hydr)oxide, in which commercially available strongly alkaline anion exchange resins of both macroreticular (Amberlite IRA 900) and gel-type structure (Amberlite IRA 402) were used as the supporting materials. The inorganic deposit was introduced into the anion exchangers in two steps conducted batchwise at ambient temperature. First, the functional groups were quantitatively transformed from the Cl^- into the $FeCl_4^-$ form using 5 mol dm^{-3} HCl solution with added $FeCl_3$. Then, the vacuum-filtered intermediate products were contacted with NaOH/NaCl solution to precipitate hydrate ferric oxides (HFO) into the grains. The matrix structure of the anion exchanger significantly affected the kinetics of the ion exchange reaction. The final products contained about 12.6% Fe. The distribution of the inorganic deposit in the two products was different (SEM, EDS analysis). Freeze drying was tried as a post-processing method to prevent the collapse of the structure of the macroreticular HIX. It was demonstrated that the way of drying (thermal drying or freeze drying) of the macroreticular anion exchanger and the HIX of the same polymeric structure had an effect on the results of the surface area and porosity measurement of both materials (determined by N_2 adsorption-desorption method and mercury intrusion porosimetry). The obtained materials will be used as sorbents for treating contaminated waters. Moreover, the results of this work will be helpful in the synthesis of HIX containing nanostructured binary metal oxides to obtain sorbents with enhanced sorption properties.

1. Introduction

Hybrid ion exchangers (HIX) are reagents which play a vital role in environment protection. They form of a subgroup of hybrid polymers in which synthetic ion exchange resins are carriers of inorganic species. Currently, because of their affinity to many species, low cost, easiness to obtain and environmental friendliness, hydrated ferric oxides (HFO) are the most studied constituents of HIX [1]. A cation or anion exchanger plays the role of a water-swelling porous carrier for the HFO deposit. The dispersion of HFO into the matrix of the supporting polymer (having a large specific surface area) prevents the agglomeration of ultrafine HFO particles and ensures a large area of contact between the reagents in the processes of catalysis and sorption. Thanks to the suitable physical form (spherical beads) HIX can be used (on the contrary to the parent HFO nanoparticles) in dynamic conditions in fixed bed column systems [2–5].

HFO can be introduced into the structure of both (sulfone and carboxyl) cation exchangers [6,7] and (strongly and weakly alkaline) anion exchangers [8,9]. The (cation- or anion-exchangeable) functional groups of the ion exchangers take part in the deposition of HFO in the sorbent and affect the course and efficiency of the sorption process. Anion exchangers containing HFO deposits are especially suitable for removing dangerous contaminants (oxyanionic pollutants) from water. The presence of electropositive functional groups in the anion exchanger structure favours the migration of the anions present in water deep into the polymeric phase, enabling their sorption into HFO (the Donnan membrane effect) [10]. Among the anions present in natural waters inorganic arsenic species pose the greatest hazard to people's health. They occur in natural waters constituting sources of drinking water in many regions of the world. Many studies have shown that HFOs immobilized and dispersed in HIX particles are effective materials for arsenic sequestration from water [11–13].

HFO particles can be loaded into the anion exchanger structure in several ways: (a) an anion exchanger with functional groups in the MnO_4^- form is brought into contact with $FeSO_4$ solution (to oxidize Fe (II) to Fe(III)) and then $Fe(OH)_3$ is precipitated with NaOH solution [14,15]; (b) the anion exchanger is impregnated with $FeCl_3$ solution in alcohol and then treated with NaOH solution [16]; and (c) an anion

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exchanger with functional groups in the $FeCl_4^-$ form is introduced into NaOH solution and the resultant beads are subjected to thermal treatment at 50–60 °C [17].

The tetrachloroferrate ion, formed in the $FeCl_3$ solution in the presence of an excess amount of hydrochloric acid or chloride salt, was effectively used for regeneration of the anion exchanger doped with the ClO_4^- ion or other strongly held anions [18]. The $FeCl_4^-$ ion is one of the anions most strongly extracted from HCl solution by anion exchangers. As the Cl^- concentration in the solution is decreased or the pH is increased, the $FeCl_4^-$ ion desorbs from the resin and decomposes to positively charged Fe(III) species. This peculiar affinity of the $FeCl_4^-$ ion towards the anion exchanger functional groups (strong bonding in concentrated chloride solution and its absence in dilute solutions) has been exploited by B. Pan and his team to deposit HFO in anion exchanger D201 (Hangzhou Zhengguang Resin Co., China). Such materials have been successfully used for removal of arsenite/arsenate [17,19–21], phosphate [22,23], selenite [24], chromate [21,25], antimonate [26] and bromate [27] from waters. However, the above research works focused on the application aspects of the polymeric materials, and only sketchy information about the procedures of obtaining them was reported.

Since it is not specified in what conditions the functional groups of the anion exchanger are quantitatively transformed into the $FeCl_4^-$ form, we decided to find this out by extending the scope of our investigations in comparison with the earlier research by other authors [17,19–27]. Such investigations are needed considering that in the previous research [27] a sorbent containing only 0.04% Fe was obtained batchwise using a solution of 0.3 mol dm^{-3} $FeCl_3$, 0.2 mol dm^{-3} HCl and 0.4 mol dm^{-3} NaCl. Therefore it is worthwhile to determine the reaction medium composition ensuring that the ion exchange reaction is quantitative, which is a prerequisite for a high HFO content in the end product. Thus, the aim of this research was to optimize the conditions of obtaining HFO-containing HIX from both macroreticular and gel-type anion exchangers and to extend our knowledge about the structure and physicochemical properties of the obtained materials. We wanted to answer the following questions. (a) In what conditions does the quantitative transformation of the functional groups of the anion exchangers into the $FeCl_4^-$ form occur? (b) What portion of the iron bonded by the functional groups remains in the ion exchanger phase after the alkalization of the reaction medium? (c) Does the structure of the anion exchanger affect the distribution of HFO in the grains? (d) Is freeze drying a cost-effective method of removing moisture from this kind of materials (containing a large amount of hydrated iron oxides)? (e) What effect does the way of drying the investigated polymeric materials (the macroreticular structure) have on the results of the surface and porosity measurements? The answers to the above questions will be helpful in the synthesis of HIX containing nanostructured binary oxides.

2. Materials and methods

The polymer support for HFO was Amberlite IRA 900 and Amberlite IRA 402–the commercial anion exchange resins produced by The Dow Chemical Co. All the chemicals used in this study, including $FeCl_3·6H_2O$, $CH_3COONa·3H_2O$, ethyl alcohol 99.8%, analytical weighted amount of di-sodium wersenate (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.

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 was placed in a conical flask and treated with 10 cm^3 of 0.5 mol dm^{-3} $FeCl_3$ in HCl solution with a concentration from 2 mol dm^{-3} to 5 mol dm^{-3}. The reagents were shaken at 20 °C for 1 h (An/Cl^- macroreticular structure) or for 1–120 h (An/Cl^- gel structure). The vacuum-filtered off intermediate product was introduced into 1 mol dm^{-3} NaOH in 1 mol dm^{-3} NaCl solution (50 cm^3) and was shaken at 20 °C for 24 h. The sediment was removed through decantation and the filtered off product, after washing with deionized water, was dried in a chamber dryer at 40 °C for 24 h.

The Fe content in the products was determined after dissolving HFO in acid solution. A sample weighing about 0.3 g was treated with 5 cm^3 of 2–6 mol dm^{-3} HCl in a conical flask and shaken for 1–3 h. After this time the polymer grains were filtered off and washed with deionized water. Then the solution was alkalized with sodium acetate and titrated with 0.05 mol dm^{-3} di-sodium wersenate against salicylic acid (2% solution in ethanol).

Microscopic examinations were performed by means of a HITACHI S-3400N scanning electron microscope (SEM) equipped with an energy-dispersive spectrometry (EDS) microanalyzer (4 nm, BSE detector).

To analyze the surface and pore parameters of the HIX macroreticular structure, the filtered off product, after washing with deionized water, was divided into two portions and dried by applying thermal drying and freeze drying techniques. The freeze drying process was conducted by treating the materials at −80 °C for 24 h, followed by drying at pressure of 0.02 mbar for 24 h using a Labconco FreeZone Laboratory Freeze Dryer 4.5 L.

The porous characteristics of the polymeric support macroreticular structure and the corresponding hybrid polymer with HFO deposit were determined by the N_2 adsorption at 77 K and mercury intrusion porosimetry. The N_2 adsorption was conducted on a Quantachrome Autosorb IQ MP surface area and porosity analyzer, Quantachrome Instruments (p/p_0 from 0.01 to 0.96). Before adsorption measurements the samples were degassed first at 50 °C for 12 h (< 15 μm Hg) and then at 25 °C for 0.5 h (< 1 μm Hg). This method allows one to define the porosity of a material in the whole range of micro- and mesopores and a smaller range of macropores. The porous characteristics in a broad diameter range from 3.6 nm to 15 μm were determined by mercury intrusion porosimetry conducted on a Micrometrics AutoPore IV 9510 analyzer under pressure from 0.05 to 414 MPa.

3. Results and discussion

HFO was precipitated into the two types of anion exchangers in batch conditions in two steps: (a) conducting the ion exchange reaction in a strongly acidic medium to transform the functional groups into the $FeCl_4^-$ form ($An/Cl^- \rightarrow An/FeCl_4^-$) and (b) decomposing the $FeCl_4^-$ ions bonded by the anion exchanger in an alkaline medium. First, Amberlite IRA 900, a macroreticular, polystyrene/divinylbenzene, strongly alkaline anion exchanger containing quaternary ammonium groups (constituting 3.18 meq g^{-1} of the dry resin), was used as the host material for the iron(III) (hydr)oxide deposit. Proper concentrations of HCl solutions, ensuring the quantitative transformation of the anion exchanger functional groups from the Cl^- form into the $FeCl_4^-$ form, and then proper conditions for transforming the intermediate product in such a way that as much as possible of the HFO deposit remained in the ion exchanger phase, were sought:

$$FeCl_3 + Cl^- \rightarrow FeCl_4^- \tag{1}$$

$$[P] - (N^+(CH_3)_3)Cl^- + FeCl_4^- \rightarrow [P] - (N^+(CH_3)_3)FeCl_4^- + Cl^- \tag{2}$$

$$[P] - (N^+(CH_3)_3)FeCl_4^- + 3OH^- + Cl^- \rightarrow [P] - (N^+(CH_3)_3)Cl^-\#FeOOH + 4Cl^- + H_2O \tag{3}$$

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

Since $FeCl_4^-$ ions form exclusively in media with a high Cl^- content (1), a series of concentrated HCl solutions (2–5 mol dm^{-3} HCl) with $FeCl_3$ (a precursor of $FeCl_4^-$) was prepared. The dark orange solution samples were shaken with anion exchanger samples (2). After a few minutes the cream-colored anion exchanger grains turned dark yellow. After 1 h the grains were vacuum filtered in order to separate as much as possible of the water phase from them. The grains could not be