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Synthesis and characterization of hybrid materials containing iron oxide for removal of sulfides from water

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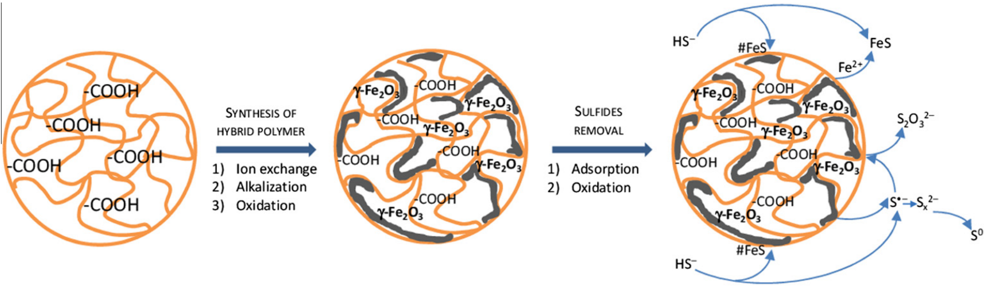
GRAPHICAL ABSTRACT



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ABSTRACT

Hybrid materials containing iron oxides based on macroporous and gel-type sulfonic and carboxylic cation exchangers as supporting materials were obtained. Multiple factors, including the kind of functional groups, ion exchange capacity, and polymer matrix type (chemical constitution and porous structure), affected the amount of iron oxides introduced into their matrix (7.8–35.2% Fe). Products containing the highest iron content were obtained using carboxylic cation exchangers, with their inorganic deposit being mostly a mixture of iron(III) oxides, including maghemite. Obtained hybrid polymers were used for removal of sulfides from anoxic aqueous solutions (50–200 mg S^{2-}/dm^3). The research showed that the form (Na^+ or H^+) of ionic groups of hybrid materials had a crucial impact on the sulfide removal process. Due to high iron oxide content (35% Fe), advantageous chemical constitution and porous structure, the highest removal efficiency (60 mg S^{2-}/g) was exhibited by a hybrid polymer obtained using a macroporous carboxylic cation exchanger as the host material. The process of sulfide removal was very complex and proceeded with heterogeneous oxidation, iron(III) oxide reductive dissolution and formation of sulfide oxidation and precipitation products such as iron(II) sulfides, thiosulfates and polysulfides.

1. Introduction

Sulfides ($H_2S_{(aq)}$, HS^- and S^{2-}) are considered to be among the most undesirable and troublesome contaminants of various aqueous environments. When present in water even at negligible levels, sulfides are distinctly perceptible and give water an obnoxious taste and odor, making it useless for municipal use in organoleptic respects. Water containing sulfides should also not be used for industrial purposes. Sulfides in the form of $H_2S_{(aq)}$ have a toxic influence on microbes performing fermentation processes. They are also reactive toward metals and metal oxides, which are active ingredients of numerous catalysts, and as a result shorten

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the time of their utilization or completely deactivate them. Moreover, if present in industrial water, sulfides have corrosive effects on pipelines, steam boilers, and heat exchangers. Since sulfides can be emitted from the solution in the form of toxic hydrogen sulfide, their presence in aqueous solutions constitutes a serious risk to human life and health [1]. Therefore, the concentration of sulfides in wastes drained away to natural water reservoirs has to be kept at a very low level (e.g. below 0.2 mg/dm^3). Sulfides are, inter alia, constituents of wastewaters from coke and steel production processes, refining of petroleum products, pulp and paper production, and tanning of raw hides. Sulfides are also formed in the natural environment as byproducts of degradation of organic matter and metabolic activity performed by sulfate reducing bacteria. These processes are ubiquitous and take place in anaerobic conditions in environments such as municipal, industrial (e.g. from meat processing) and agricultural wastes (e.g. in liquid manures). Sulfides are also constituents of one of the renewable fuels, biogas (up to 0.4% v/v H_2S), which therefore has to be desulfurized before use [1,2].

There are some well-known methods used for removal of sulfides from industrial wastewaters. The simplest of them is to lower the pH and drive away sulfides from the solution in the form of hydrogen sulfide with air (at pH ~5.0 sulfides are present in aqueous solutions only in the molecular form of $H_2S_{(aq)}$) followed by its absorption in alkaline media or adsorption on bog ore. Sulfides can also be oxidized in the solution by means of low-molecular weight oxidizers, such as chlorine and its compounds, oxygen, ozone, hydrogen peroxide or potassium manganate(VII). It is also possible to precipitate sulfides using iron(II) or iron(III) salts. Nevertheless, basic approaches for sulfide removal are usually not suitable to completely remove sulfides from aqueous solutions. Therefore after the treatment there are some microquantities of sulfides left that can cause technical problems and are a source of odor [1,3,4].

Adsorption processes are a well-established technology which is highly valuable for removal of contaminants present in wastewater streams in low concentrations. However, the most widely used adsorbent – activated carbon – exhibits low selectivity towards sulfides and requires modification before use [5,6]. Recent research in this area has also focused on the use of metal oxides as adsorbents for removal of residual sulfides. Metal oxides such as iron (III), manganese(IV), copper(II), and zinc(II) oxides are considered to show adequate reactivity toward sulfides (being able to oxidize/adsorb them) in aqueous environments. Currently Fe(III) oxides have significant practical relevance, mostly because they are non-toxic, cheap, and easy to obtain, they are also often constituents of hard to reuse industrial wastes (adsorbents with iron (III) oxides are widely used for desulfurization of biogas). However, the process of chemisorption of sulfides by means of reactive metal oxides has some serious drawbacks, in particular when powdered metal oxides are used. These oxides tend to agglomerate in aqueous solutions, and in consequence their active surface area is considerably decreased. Moreover, separation of metal oxide suspended matter after the process is also considered a serious technical problem [4].

In order to prevent technical problems associated with agglomeration and separation of iron oxides during and after the water purification process, the particles of iron oxides are deposited in the structure of porous, water-insoluble, chemically resistant carriers (such as silica, montmorillonite) and organic polymers (e.g. cellulose or ion exchangers) [7–10]. Ion exchangers are particularly good raw materials for producing these types of hybrid adsorbents, since they are characterized by large surface areas, a well-developed pore structure and the presence of ionic functional groups (through which an inorganic deposit can be introduced into the structure of an organic polymer). Among them, various reactive functional polymers including anion exchangers [11,12] cation exchangers [13–16] and macromolecular oxidizers [17] were used as polymeric supporting materials for iron oxide deposition. Iron oxide precipitation within the structure of a polymeric matrix containing different functional groups and porous characteristics makes the process more complex than precipitation conducted in the solution. Therefore using different methods of synthesis and supporting polymers, products containing different polymorphic forms of iron oxides (magnetite, maghemite, ferrihydrite, amorphous hydrous iron oxide) with different iron content were obtained. Through conversion of the macroporous sulfonic cation exchanger into the Fe^{2+} form and then through alkalization with NaOH solution and oxidation with H_2O_2, Ziolo et al. obtained a hybrid polymer with adequate optical properties containing iron oxides in the form of maghemite [13].

In the present study the same method of iron oxide deposition within the matrix of different carboxylic and sulfonic cation exchangers was used. Since the properties of the products may depend not only on the reactions used to produce them, but also on the properties of polymer matrix, the partial aim of the present work was to determine the influence of ion exchange capacity, chemical constitution and the morphologic structure of cation exchangers on the form and quantity on iron oxide deposit. Simultaneously, the structure of iron oxide and distribution of its deposition within polymer matrix, and properties of the polymeric support, may have a significant bearing on sorption capacity of the obtained products. Since, to the best of the authors' knowledge, these types of materials were not used for removal of sulfides from aqueous solutions, the aim of this study was to evaluate adsorption/oxidation properties of the hybrid polymers containing iron oxide obtained using different cation exchangers as the host polymers.

2. Experimental section

2.1. Materials

The polymeric support for dispersed iron oxide were cation exchange resins being commercial products sourced by Dow Chemicals. The characteristics of these materials are described in Table 1. SM, SG, CM and CG stand for respectively a macroporous cation exchanger with sulfonic acid functional groups, a gel-type cation exchanger with sulfonic acid functional groups, a macroporous cation exchanger with carboxylic acid functional groups and a gel-type cation exchanger with carboxylic acid functional groups.

2.2. Synthesis

The ion exchangers used in all the syntheses were in the Na^+ form. Encapsulation of iron oxide within the polymer matrix was

Table 1
Characterization of polymeric support.

Property	Amberlite 252	Amberlite IR120	Amberlite IRC50	Amberlite IRC86
Matrix[a]	S/DVB	S/DVB	PA/DVB	PA/DVB
Matrix structure	Macroporous	Gel	Macroporous	Gel
Functional group	$-SO_3Na$	$-SO_3Na$	$-COOH$	$-COOH$
Exchange capacity (meq/g)	4.3	4.4	10.8	10.7
Appearance	Beige, opaque	Yellow, translucent	Creamy, opaque	Brownish-red translucent
Code	SM	SG	CM	CG

[a] S/DVB – Styrene–divinylbenzene copolymer, PA/DVB – Polyacrylic-divinylbenzene-copolymer.