Microporous and Mesoporous Materials 248 (2017) 222–233

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Structure investigation of nano-FeO(OH) modified clinoptilolite tuff for antimony removal

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ARTICLE INFO

Article history:
Received 8 December 2016
Received in revised form
6 April 2017
Accepted 12 April 2017
Available online 14 April 2017

Keywords:
Adsorption
FeO(OH) species
Goethite
Ferrihydrite
Magnetite
Hematite
Antimony removal

ABSTRACT

Biomimetic sol-gel synthesis was used to prepare new FeO(OH) zeolite (clinoptilolite tuff) adsorbent effective for antimony removal. The product was compared with other on the market accessible natural or commercial adsorption materials like granulated ferric hydroxide GEH, powder of zero valent iron (ZVI)- nanofer and the new synthesized oxi(hydr)oxide FeO(OH) and characterized by XRD, XPS, Raman, FT IR, TG, DTA, DTG, TEM and SEM techniques. Based upon the SEM analysis, the oxidized nanofer sample revealed the existence of hematite and goethite and morphology of FeO(OH) dopant confirmed the presence of ferrihydrite, in less extent also magnetite and hematite. Recorded exothermic maxima on DTA curves for powdered FeO(OH) zeolite at 460 °C and for pure component FeO(OH) at 560 °C indicated an 100 °C shifted exothermic effect, which characterized strong chemical interaction of FeO(OH) with zeolite structure. Based upon the XPS analyses, also the difference between Fe species in the raw and FeO(OH) doped zeolite was found in increasing Si/Al ratio, however only at the surface below app. 5 nm, measured as 3.94 for raw and 5.38 for sample treated with alkalic solution. The plotting of adsorption isotherms in the system studied clearly showed the increasing uptake capacity of the adsorbents towards antimony with the increased S(BET) data (GEH ˃FeO(OH)˃FeO(OH) zeolite˃nanofer).

1. Introduction

Inspiration from nature has been widely used in the development of new materials and in the improvement of their properties since long time. Superhydrophobic surfaces inspired in species present in nature with highly water repellent self-cleaning properties, such as the well-known lotus leaf, are interesting examples of the biomimetic approach for the development of affordable materials and state-of-the-art techniques. The most progressive tissue engineering in regenerative medicine, gene therapy, drug encapsulation and other promising research results are known today [1–3].

Materials designed using components derived from biological sources such as collagen, chitosan, three-dimensional polymeric hydrogels like surfactants, alginate, plant proteins and polysaccharides have also been investigated thoroughly for use in environmental adsorbents fabrication. Natural biomaterials possess some advantages over their synthetic counterparts, such as their capability to be environmentally viable and thus recognized by the living microenvironment. Since the beginning of 21st century, several types of hydrogels with excellent mechano-chemical properties have been developed through applying different synthesis routes. Biomimetic sol-gel strategy presents the most frequently used synthesis route in advanced adsorbents fabrication [4–6].

When iron is stored as a nanoparticle of iron oxide (ferrihydrite) inside the protein cage ferritin (Fn), it is completely sequestered

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http://dx.doi.org/10.1016/j.micromeso.2017.04.022
1387-1811/

and rendered inert. Thus the encapsulation and sequestration of the iron oxide nanoparticle in biological systems highlights its tremendous potential for use as a synthesis platform for material design. From understanding direct biomineralization in Fn, scientists developed a model for surface-induced metal oxide formation and have used this as a guiding principle for the synthesis of metal oxide nano-particles in other natural or engineered architectures [7–10].

Recent literature dealing with tectosilicates valorization reports state of the art mainly in their external surface modification using the sol-gel technique, surfactants coating, deposition of zero valent iron ZVI, silver clusters, iron oxihydroxide nanoparticles and semiconductor like titanium dioxide or their pelletizing with some biopolymeric eco-friendly carbohydrates [4–6,11–15]. Environmental requirements are becoming increasingly important in today's society, since there is an increased interest in the industrial use of renewable resources. Simultaneously, it is believed that nature's pattern may indicate that in the near future the synthesis development of traditional adsorbents might change.

Metal oxides based adsorbents are effective, low cost adsorption materials for heavy metals and other pollutants removal together with pathogen detection. Their sorption process is mainly controlled by complexation. When their particle size is reduced to below 20 nm, the specific surface area of normalized adsorption capacity increases 10–100 times, suggesting a „nanoscale effect“. They may be combined with other carriers or pelletized or enriched with a broaden range of functional groups and thus separated magnetically. Current immobilization techniques usually result in significant loss of treatment efficiency. Therefore, research is needed to develop simple, low-cost methods to immobilize nanomaterial without significantly impacting its performance. Nevertheless, to overcome a potential human risk from environmental spreading, nanomaterials need to be embedded in a solid matrix, respectively, to have minimum release until they are disposed of [6,7,10,11].

Stibnite (Sb_2S_3) dominant mines were located in various zones of the Western Carpathians of Slovakia. All Slovak Sb deposits were closed and abandoned in the early 1990s mostly without their remediation. Unfortunately, this long-term exploitation of Sb has produced in country large amounts of waste rocks and tailings which are contributing to the contamination of the surrounded environment. Waters from each mine site show no acid drainage (pH 6.2–8.2) due to neutralizing by abundant Ca- and Mg-carbonate intercalations in the mineralized rocks. As analyses revealed, also substantial amounts of Sb is associated with hydrous ferric oxides (ferrihydrite and goethite) commonly occurring at that mines and thus helping to decrease this pollution. Despite the natural attenuation processes concentration of Sb in downstream surface waters and groundwaters are remaining high, many times overpassing the drinking water limit (5 μg/L). Antimony metalloid is considered to human health toxic and carcinogenic while elemental antimony is more toxic than its salts and inorganic forms are more toxic than organic ones [14].

Therefore, the objective of this work was to use zeolite (clinoptilolite tuff) from the inland deposit Nižný Hrabovec as template or nanoreactor in more effective biomimetic sol-gel synthesis and thus to prepare new upgraded, economically feasible adsorbent FeO(OH) zeolite. The adsorbent synthesized was characterized thermoanalytically, by TEM and XRD and its FT IR, Raman, SEM micrographs and SEM-EDS records were compared with other similar products like GEH, nanofer, synthesized oxi(hydr)oxide FeO(OH) and parent (raw) zeolite. Finally, adsorption performance of the above materials towards antimony was validated by isotherms plotting.

2. Materials and methods

2.1. Adsorbents

Granulated ferric hydroxide (GEH^{104}), developed at the Department of Water Quality Control in Technical University Berlin, is an approved commercial adsorbent manufactured by GEH Wasserchemie GmbH & Co. KG Osnabrück (Germany). The main components of GEH are akaganeite (β–FeOOH) and goethite [α-FeO(OH)]. The product has the specific surface area about 220 m^2/g, water content of 45%, bulk density 1.2 g/cm^3 and the price of 3750 Euro per ton [4–8,11].

The domestic zeolite (clinoptilolite tuff, deposit Nižný Hrabovec at the eastern Slovakia) was chosen on the base of its low-price availability in the local market (15–35 Euro per ton for size-granulation of 0.2–1 mm) and due to its sufficiently large surface area in powdered form (~60 m^2/g), the highest one among the other natural products, rigidity and surface functionality. The clinoptilolite tuff examined contains a significant percentage of the active mineral, i.e. clinoptilolite (cca 85%) and is consequently classified as an excellent mineral cation exchanger. Mineralogical and chemical composition of the clinoptilolite tuff examined in this study describes literature [4,12] and Table 1.

Due to the very high price of commercial Fe-oxihydroxide (GEH) on our market which was quite frequently used for As and Sb removal from some underground water reservoirs in Slovakia we prepared and compared the chemically pretreated FeO(OH) clinoptilolite tuff with the above GEH product. Thus, 20 g of (0.2–0.8 mm) grain-sized zeolite was mixed with 0.5 L of 10% aqueous solution of iron (III) nitrate nonahydrate [$Fe(NO)_3 \cdot 9H_2O$, Alfa Aesar, crystalline, Germany] and aged at 60 °C in laboratory water bath shaker for 3 days. Then, the 200 mL of 2.5 M KOH solution was added dropwise to prepare the final suspension of pH = 12 and keeping it aged for another 6 days at room temperature. After the reaction period the suspension was filtered and washed with deionized water and finally dried at 105 °C for 2 h in laboratory dryer.

Czech commercial product nanofer 25S (Nano iron, s.r.o, Rajhrad) was used for comparing the product adsorption capacity with all other examined samples due to some similarities with its iron oxides composition especially after air-oxidation and drying. Original nanofer substance as ZVI (Zero-Valent Iron) powder was stored and supplied in certified packaging. In order to prevent undesirable transformation of Fe(0) to Fe_2O_3 ZVI was processed in dispersing apparatus under protective atmosphere. The price of above product on the market is 26 360 €/1t.

2.2. Characterization

Elemental analysis of the samples and their SEM micrographs were performed on Scanning Electron Microscope SEM, Hitachi TM 3000 with integrated EDS spectrometer (EDS Oxford Instruments Swift ED 3000). Table 1b represents an average weight percentage of the elements in individual sample calculated from 10 to 15 measurements depending on sample homogeneity.

TEM micrographs of FeO(OH) zeolite were visualized using a transmission microscope (TEM) JEM ARM 200cF working at 200 kV and by scanning electron microscope (SEM) JEOL JSM 7600F working at accelerating voltage 0.5 kV. The samples for SEM study were stuck on the double-sided adhesive tape and then carbon coated. Samples for TEM examination were firstly dispersed in ethanol using ultrasound and only a drop of suspension was placed on a carbon coated grid. After drying in the air, sample was studied in TEM.