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THE CERAMIC-LIKE SYNTHETIC COMPOSITE BASED ON FE/MN OXIDES AND $MnCO_3$ AS ADSORBENT FOR THE REMOVAL OF TOXIC ANIONS, SUCH AS ARSENITE AND SELENITE

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Abstract. This work presents the synthesis and characterization of the ceramic-like inorganic composites based on Fe/Mn oxides and Mn(II) carbonate, and explores their application in adsorptive removal of toxic anions from water. The composites of several Fe-to-Mn ratios were prepared via the urea-supported hydrothermal precipitation approach and further treated at 80 and 300 ºC. The obtained materials were tested for their adsorptive removal of the list of target (for water treatment) anions. The sample having the best performance (the greatest affinity for) to arsenite (H_3AsO_3) and selenite ($HSeO_3^-$) was chosen and further investigated as anion exchanger for these anions. The molecular-mechanism of As(III) and Se(IV) adsorption was studied by a number of spectroscopic methods. The possibility of using the best composite sample (based on Fe^{3+}/Mn^{3+} oxides and $MnCO_3$) under dynamic adsorption conditions (industrial choice of adsorption technology) was confirmed by testing the material performance in adsorption columns.

Key words: composite based on Fe/Mn oxides and $MnCO_3$; inorganic anion exchangers; adsorption; urea-supported hydrothermal synthesis; arsenite; selenite; water purification.

Over the last decades, natural and synthetic complex metal oxides and composites on their basis are widely explored in high technologies (catalysis, energy, medicine etc.) due to their well-known advantages compared to the respective individual metal oxides. The first two commercially available anion exchanges were based on individual metal oxides: Al_2O_3 (activated alumina) and Fe_2O_3 (granular ferric hydroxide); they came into water market in 2004-2006 to solve the problem of the (first of all) arsenic contamination in drinking water. Since then, the society and most drinking water plants demand new anion exchangers having better performance and a broader spectrum of applicability. Trying to satisfy these request/expectations, adsorption material scientists have also switched their attention to complex metal oxides. It was proved that adsorption characteristics of such inorganic composites exceed those of individual metal oxides.

Responding to the needs above, we decided to develop several series of inorganic composites based on two-metal oxides and to find their application in adsorptive removal of specific anions, whose maximum contents is strictly controlled by the World Health Organization (WHO) via establishing maximum permissible concentrations (MPC) in drinking water. One of the series of such complex structure ceramic-like adsorbents (that we produced) were the composites based on Fe/Mn oxides. Thus, the goal of our research was to: synthesize new inorganic anion exchangers based on oxides of Fe and Mn; verify their performance to the list of anions using the quick one-point sorption tests; select the most appropriate pairs: adsorbent-adsorbate; characterize the structure/surface of the best samples; investigate their adsorption properties deeper in static and dynamic conditions; reveal the molecular-level mechanism using several spectroscopy methods. Note: The physical and physico-chemical properties to be provided to such ceramic-like composite (as studied in this work) for application in adsorption technology must be different (opposite) compared to that used for traditional application of ceramics (clay tile and brick, china tableware, refractory linings, and industrial abrasives). Here, we look for porous materials with highly reactive surface, capable for selective removal of specific ions from water.

The Fe/Mn oxide-based composites were produced by the urea-supported hydrothermal synthesis in autoclave {versoclave of the type 3E/3.0 lt (60 bar. N 5896) using an Autoclave Suurmond BV (Büchi Glas Uster AG, Switzerland)} [1]. We anticipated that this synthetic method will endow with the wanted properties to the materials, in particular: porosity, heterogeneity, high surface reactivity and a variety of surface adsorption sites. The preparation approach is grounded on the decomposition of urea {$CO(NH_2)_2$} which results in the release of OH^- and CO_2 in solution {both of which will contribute to the desired material chemical composition (metal oxides) and properties} according to the reaction (1): $(NH_2)_2CO + 3H_2O \rightarrow 2NH_4{\cdot}OH + CO_2$ (1)

In a typical synthesis, a mixture of the precalculated quantities of powders of $FeSO_4{\cdot}7H_2O$, $MnSO_4{\cdot}H_2O$ and $CO(NH_2)_2$ (0.12, 0.12 and 0.64 mol, respectively) were dissolved in 2800 mL of distilled water. The solution was placed in a 3000 mL autoclave and maintained at 120°C for 24 h at the rotation of 750 rpm. The autoclave was switched off and left to cool down to the ambient temperature. The formed precipitate was filtered; thoroughly washed with distilled water and rinsed with alcohol. Finally, the materials were dried first at 22°C and then at 80°C and 300°C. This way, the six samples composed of Fe and Mn oxides were prepared: Fe1/Mn2-80; Fe1/Mn2-300; Fe1/Mn1-80; Fe1/Mn1-300; Fe2/Mn1-80; Fe2/Mn1-300, where 80 or 300 is the treatment temperature; 1 or 2 is the ratio of Fe-to-Mn in the initial precursor [1-4].

We did not plan a deep characterization of all samples. Instead, we first run the quick adsorption (one-point) tests for the following anions: $H_2AsO_4^-$, H_3AsO_3, SeO_4^{2-}, $HSeO_3^-$, $H_2PO_4^-$, F^-, Br^- BrO_3^-, H_3BO_3, $HCrO_4^-$, and then selected the best sample (from the list of the six composites) for each of these anions, taking into account that the material shall be stable enough in water. Having applied such a search approach, we continued working with the composite of the Fe-to-Mn ratio of 1:1, treated at 300ºC, as this material demonstrated a very competitive removal of As(III) and Se(IV) and excellent performance (easy-to-use) in dynamic sorption [1-4].

The structure and surface chemistry of the selected composite were characterized using X-ray diffraction patterns (XRD), N_2 adsorption/desorption isotherms, thermogravimetric analysis (TGA), infra-red spectroscopy (FTIR), zeta-potential measurements, potentiometric titration, X-ray photoelectron spectroscopy, scanning electron microscopy (SEM) [1, 2]. Table 1 presents the main properties of the Fe/Mn oxide-based composite used in this work [2]. Figure 1 shows the morphology in SEM picture (A) and the XRD patterns of the material [2]. The XRD detected the highly crystalline phases in the Fe/Mn oxide-based adsorbent: rhodochrosite, $MnCO_3$ (JCPDS Card 83-1763) and subordinate maghemite, γ-Fe_2O_3 (JCPDS: Card 24-81), Figure 1;

in addition, it contained the amorphous phases of Fe^{3+} and Mn^{3+} hydrous oxides as confirmed by the FTIR and XPS spectra [1].

Table 1. The physico–chemical properties of the Fe–Mn based adsorbent [2]. Reproduced/adapted from [Szlachta M., Chubar N. (2013) The application of Fe-Mn hydrous oxides based adsorbent for removing selenium species from water. *Chem. Eng. J.* 217, 159-168.] Copyright [2024] [Elsevier].

BET surface area (m^2/g)	124	Apparent density (g/cm^3)	1.4
Pore volume (cm^3/g)	0.095	TGA weight % loss at 105 °C	4.28
Average pore diameter (nm)	2.51	TGA weight % loss at 450-1000 °C	12.92
Particle size d_{50} (μm)	17.0	pH_{pzc}	4.5
True density (g/cm^3)	4.1	Anion exchange capacity (mgeq/g)	3.73

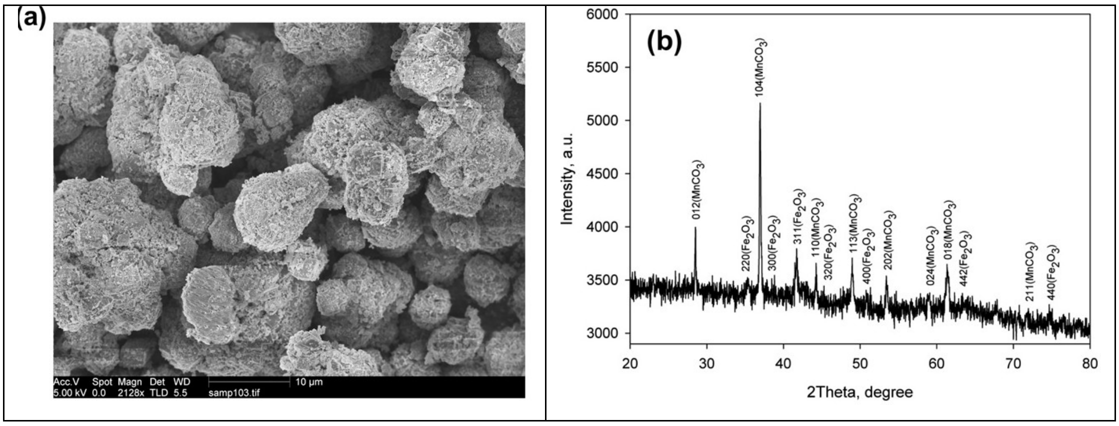

Figure 1. The SEM image (a) and XRD patterns (b) of the composite based on Fe-Mn hydrous oxides [2]. Reproduced/adapted from [Szlachta M., Chubar N. (2013) The application of Fe-Mn hydrous oxides based adsorbent for removing selenium species from water. *Chem. Eng. J.* 217, 159-168.] Copyright [2024] [Elsevier].

The sorption properties of the Fe/Mn oxide-based composite to arsenite and selenite were thoroughly characterized under static (isotherms; kinetics; effect of pH, adsorbent dose and competing anions) and dynamic (in columns) experimental conditions [1, 2]. Figure 2 reflects the adsorption capacities of the material to arsenite and selenite determined from the equilibrium adsorption isotherms built within the pH range of the purifying drinking water (pH=6.5-8.5) [1, 2]. The very competitive and attractive adsorption {almost pH independent for As(III)} is correlating with the high rate kinetics of the removal and a minor influence of the competing anions [1, 2].

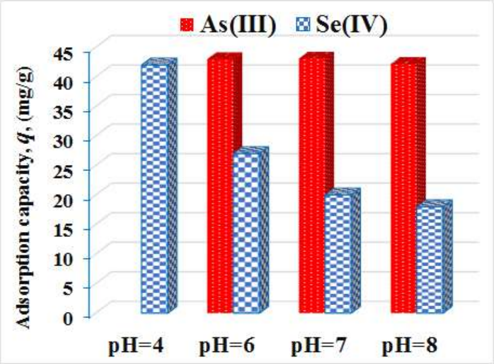

Figure 2. The adsorption capacities of the Fe/Mn oxide-based composite to As(III) and Se(IV) drawn from the equilibrium isotherms shown in [1, 2]. The new figure built using the data of [1, 2].

The experimental data were described (fitted) well to the Langmuir model (isotherms) and the pseudo-order adsorption kinetics, both of which indicate the chemisorption of the As(III) and Se(IV) uptake. The molecular-level mechanism of the selenite adsorption on the Fe/Mn oxide-based composite was studied using Extended X-ray absorption fine structure (EXAFS), X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR) [3]. This allowed us to discover the type of the inner-sphere surface complexation of $HSeO_3^-$ on the Fe/Mn oxide-based adsorbent, as well as the phases of this composite involved in the uptake at various pH values, see details in [3].

CONCLUSIONS

The new ceramic-like composite based on Fe/Mn oxides and $MnCO_3$ was developed using the urea-supported hydrothermal precipitation method. The structure and surface chemistry of this material {consisting of the highly crystalline phases of rhodochrosite ($MnCO_3$) and subordinate maghemite (γ-Fe_2O_3), as well the amorphous hydrous oxides of Fe^{3+} and Mn^{3+}} were characterized, and its adsorption properties to aqueous As(III) and Se(IV) anions were determined under the static and dynamic experimental conditions. The inorganic composite adsorbent demonstrated a very competitive and technologically attractive (pH independent for aqueous As^{3+} within the relevant pH range) removal capacity of $HSeO_3^-$ and H_3AsO_3 ranged 18-41 mg[Se]/g and 40-42 mg[As]/g, respectively. The removal rate of these anions by the Fe/Mn oxide-based composite was one of the highest compared to the literature, which makes this material a promising anion exchanger for industrial scale application.

The Fe/Mn oxide-based composite is the mechanically strong sample, stable in water and easy-to-use under dynamic adsorption in columns without granulation. It is capable to purify several hundreds of bed volumes of water solutions containing Se(IV). Such outstanding adsorptive properties of the investigated composite are due to the chemisorption mechanism of Se(IV) removal, realized via the formation of bidentate binuclear (corner-sharing) ^2C complexes of $HSeO_3^-$ to the Fe/Mn oxides octahedra. The amorphous Fe^{3+} oxides were the main selenite removal phases followed by the amorphous Mn^{3+} oxides. Due to the presence of the above compounds, both the highly crystalline phases ($MnCO_3$ and γ-Fe_2O_3) did not contribute to the anion uptake.

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References:

1. Szlachta M., Gerda V., Chubar N. (2012) Adsorption of Arsenite and Selenite Using an Inorganic Ion Exchanger Based on Fe-Mn Hydrous Oxide. J. Colloid Interface Sci., 365(1), 213. https://doi.org/10.1016/j.jcis.2011.09.023
2. Szlachta M., Chubar N. (2013) The Application of Fe-Mn Hydrous Oxides Based Adsorbent for Removing Selenium Species from Water. Chem. Eng. J., 217, 159. https://doi.org/10.1016/j.cej.2012.11.100

3. Chubar N., Gerda V., Szlachta M. (2014) Mechanism of Selenite Removal by a Mixed Adsorbent based on Fe-Mn Hydrous Oxides Studied using X-ray Absorption Spectroscopy. Environ. Sci. Technol., 48, 13376. https://doi.org/10.1021/es503606j
4. Chubar N., Szlachta M., Gerda V. (2023) Extended X-ray Absorption Fine Structure Revealed the Mechanism of Arsenate Removal by the Fe/Mn Oxide-based Composite under Conditions of Fully Saturated Sorption Sites. ACS Appl. Mater. Interfaces, 15, 44572. https://doi.org/10.1021/acsami.3c10999