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NEW MATERIALS FOR REMOVING NITRATE, MANGANESE AND IRON FROM GROUNDWATER

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Introduction

Classical methods used to remove pollutants from groundwater are known to be generally expensive and with a high potential to generate by-products or waste. In this respect, an increasing attention has been paid to obtaining, characterization and testing of new environment-friendly materials and technologies that can be successfully applied in groundwater treatment without a negative impact on them. The removal of nitrate, manganese and iron from groundwater using clean technologies is an example in this area.

Iron is one of the most abundant metals in the Earth's crust and it is generally found together with manganese. These are used widely in many applications like primary cells, alloys industry, ceramics, electrical coils, etc. Above specific levels, iron and manganese can pose an unfavourable impact to both the environment and human beings (Nuratiqah et al 2018, Zhanga et al 2019, Bacquart et al 2015, Yang et al 2019). Both iron and manganese ions are found in surface and groundwater at fluctuating concentration levels. They give water a metallic taste and serve as substrates for the growth of bacteria in water mains. They are also present in the atmosphere as suspended particulates due to its disposal from different sources like industrial emission and soil erosion (Shafiquzzaman 2017, Nasir et al 2019).

Several techniques were employed for the pollution abatement with metal ions in water which include adsorption (Nasir et al. 2019), chemical precipitation (Štembal et al 2005), ion exchange (Cheng et al. 2017), biosorption (Li et al 2019), membrane filtration (Vries et al 2017), coagulation-flocculation (Du et al 2017), and flotation (Stjepanović et al 2019). Many of these techniques have disadvantages. For example, precipitation can be considered as the most economical valid, but additional treatment is required due to the production of precipitate sludge. Reverse osmosis, ion-exchange, and other membrane separation techniques can efficiently be used in metal ions removal, but there are limitations in the use of these techniques such as expensive materials and high functional cost.

The iron based nanoparticles such as magnetite (γ-Fe_2O_3) and magnetite (Fe_3O_4) have gained increasing attention due to their unique chemical properties resulting from different iron oxidation states. The simplicity with which these nanoparticles are prepared and the stability they provide are also important aspects that have contributed to the popularity of these materials. Both of them have the ability to adsorb chemical species through physical and chemical mechanisms. Recently, the iron based nanoparticles have been subjected to functionalization with different organic molecules in order to improve their performances such as colloidal dispersibility and adsorption capacity for different chemical species.

The increased NO_3^- concentration in public water supplies presents a potential health hazard due to the nitrites reduction in the gastrointestinal tract. In its turn, NO_3^- is a potential health hazard to infants (Fish 2009, Djouadi Belkadaa 2018) and pregnant women due to NO_3^- reduction to NO_2^- , in the infants stomach, which can bind with the hemoglobin of the affected babies, thus diminishing the oxygen transfer to the body's cells resulting in a bluesh skin color often called methemoglobinemia or "the blue baby syndrome" (Zhang et al 2018, Clague et al 2019).

Therefore, the objective of this work was to obtain, characterize and test a functionalized magnetite that could be effective, both economically and technically, in the treatment of groundwater containing manganese, iron, and nitrates. Thus, the experiments have focused on materials like magnetite (Fe_3O_4) and ethylenediaminetetraacetic acid (EDTA)/magnetite (Fe_3O_4).

Materials and methods

Preparation of Fe_3O_4 and Fe_3O_4/EDTA

The chemical reagents used for the synthesis of EDTA-functionalized Fe_3O_4 nanoparticles were iron (II) sulphate (Merck), iron (III) chloride hexahydrate (Aldrich), ammonium hydroxide solution of approximately 25% by weight (Merck), and EDTA (Merck). The materials were synthesized by the co-precipitation method.

In this respect, Fe_3O_4 ($FeO \cdot Fe_2O_3$) was obtained directly by the precipitation reaction of Fe (II) and Fe (III) salts with concentrated ammonia without heat treatment. In this respect, the required stoichiometric amounts of the two solutions ($FeSO_4$ and $FeCl_3$), calculated to obtain $2.5 \cdot 10^{-3}$ moles of Fe_3O_4, were introduced into a reaction vessel. Subsequently, 15 mL of concentrated ammonia is added to the reaction vessel with continuous stirring. The reaction mixture is stirred for an additional 15 minutes until a black precipitate is obtained. The obtained precipitate was immobilized at the bottom of the vessel by a magnet placed under the glass, after which the solution above was removed. The precipitate was washed three times with approximately 25 mL of distilled water until the complete removal of the chloride ions, and then it was transferred to a pre-weighed watch glass to get dried. After drying the yield of the magnetite production was determined. The presence of chloride ions in the wash water was checked with silver nitrate solution.

In the second step, the EDTA-functionalized Fe_3O_4 nanoparticles were synthesized by using the same procedure used for the synthesis of the Fe_3O_4 nanoparticles. In this case, 50 mL of a 0.002 mol/L EDTA solution was added to the reaction vessel soon after the ammonium hydroxide was added. The reaction mixture was stirred for one hour at 50 °C, after which the precipitate obtained was washed three to four times with approximately 25 mL distilled water until complete removal of chloride ions. Finally, the precipitate was dried at 80 °C for three hours. The obtained compositional formulations were characterized through TGA/DSC and Fourier transform infrared spectroscopy (FTIR).

The experiments were carried out on two types of adsorbent materials namely Fe_3O_4 and EDTA/Fe_3O_4 at a mass ratio of 1 to 10. The granules size of the adsorbent materials ranged from 0.001 to 1.5 mm. The adsorption experiments consisted of contacting the adsorbent materials with nitrates, iron, and manganese aqueous solution with a concentration of target species ranged from 5-100 mg/L for 2.5, 5, 10, 15, 20, 30, 40, 50, 60 minutes. At the end of each contacting time the sample were filtered and measured for the species of concern.

Results and conclusions

Fe_3O_4 and EDTA/Fe_3O_4 characterization

The obtained materials were characterized by Fourier transform infrared spectrometry (FTIR) and thermogravimetric (TGA). In this respect, the FTIR spectra (Figure 1) show peaks for N-H (3228 – 3369 cm^{-1}), C=O (1625 – 1628 cm^{-1}), C-N (1432 – 1433 cm^{-1}), and C-NH_2 (1111 – 1114 cm^{-1}), and Fe-O (413 – 533 cm^{-1}). The new peaks appearing in the EDTA/Fe_2O_3 spectrum, namely C-C (860 cm^{-1}), [N(-CH_2-)$_3$] (971 cm^{-1}), and (C-O) COOH (1369 cm^{-1}) are attributed to the functionalized EDTA molecule on the magnetic nanoparticles surface.

Comparative with the thermogram of Fe_2O_3 (Figure 2a), the thermogram of EDTA/Fe_2O_3 (Figure 2a) shows three weight loss steps which could be also associated with the presence of EDTA. The initial 3.07 % (Fe_2O_3) and 4.31% (EDTA/Fe_2O_3) weight loss at temperature bellow 200°C is attributed to the dehydration process. The weight loss between 200 and 500 °C, as can be seen in EDTA/Fe_2O_3 thermogram, is attributed to the complete decomposition of EDTA most probably through pyrolysis and oxidation. All these results suggest the EDTA was successfully attached on the surface of magnetite nanoparticles.

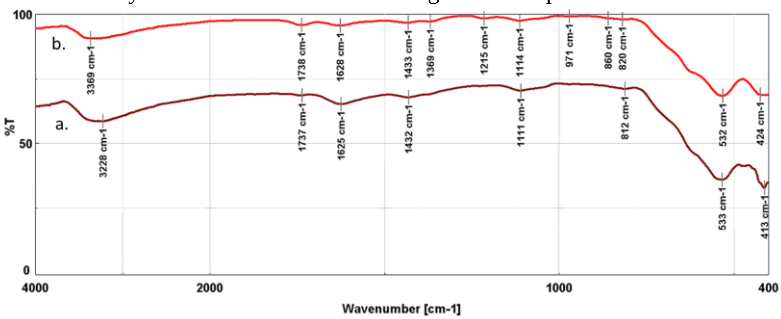

Figure 1. FTIR spectra of Fe_3O_4 (a.) and EDTA/Fe_2O_3 (b.)

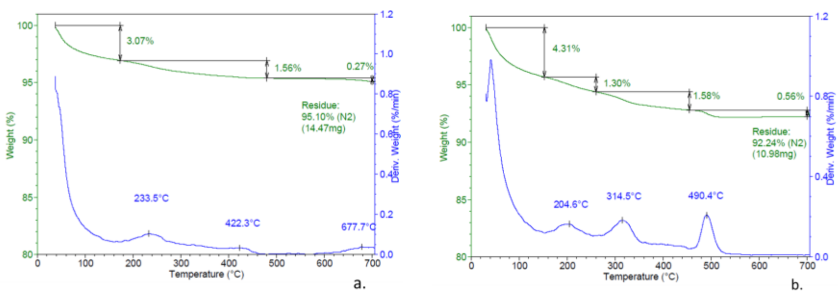

Figure 2. TGA for Fe_3O_4 (a.) and EDTA/Fe_2O_3 (b.)

Adsorption results

The results of the adsorption studies revealed that both the adsorption capacity and the degree of removal of nitrates, manganese and iron from groundwater increased sharply until a contact time of 10 minutes, after which both of them remained almost constant (Figure 3).

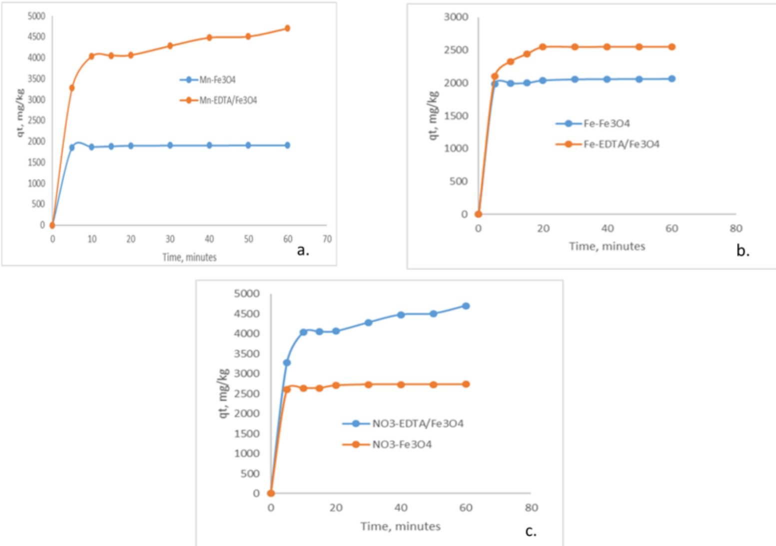

Figure 3. Adsorption of manganese (a.), iron (b.), and nitrates (c.) on Fe_3O_4 and EDTA/Fe_3O_4

The high rate of adsorption at the beginning of the process could be attributed to the existence of a large number of adsorption sites on the surface of the adsorbent at the beginning of the process. It can be observed that in all cases the equilibrium was reached after approximatelly10 minutes when more than 95% of nitrate, manganese and iron in the groundwater was removed. In terms of adsorption capacity (corresponding to the 60 minutes of contact), Fe_3O_4 has an adsorption capacity for manganese of 1910 mg/kg while, for the same metal, EDTA/Fe_3O_4 has an adsorption capacity of about 2.5 times higher, namely 4703 mg/kg (Figure 1a). As for iron, EDTA/Fe_3O_4 has an adsorption capacity of 2550 mg/kg, which comparative with that for Fe_3O_4 (2030 mg/kg) is only 1.3 times higher (Figure 2b). The adsorption capacity of Fe_3O_4 for nitrate is 2735 $mg \cdot kg^{-1}$ while, that of EDTA/Fe_3O_4 is 4703 $mg \cdot kg^{-1}$, of about 2.5 times higher (Figure 3c).

Conclusions

The objective of this work was to obtain, characterize and test an EDTA functionalized magnetite for removing manganese, iron, and nitrates ions from aqueous solutions similar to groundwater. The success of the synthesis of the new material has been confirmed by FTIR and TGA analysis that revealed new properties comparative with the basic material, namely magnetite. The adsorption experiments revealed that EDTA functionalized magnetite has a much higher adsorption capacity than magnetite, especially for manganese and nitrates. Moreover, the high rate of adsorption of the three chemical species has been highlighted. In this regard, about 95% of them were removed from the aqueous solution in about 10 minutes.

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