Magnetoactive Humic-Based Nanocomposites

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Summary: We have elaborated several approaches for the preparation of magneto-active nano-hybrid composites, including i) *ex situ* method, which consists of the precipitation of magnetic particles from Fe(II) and Fe(III) salts followed by their incorporation into the humic acids matrix and ii) a chemical precipitation method *in situ* where the magnetic particles are grown within the humic acids matrix. It was proven that adsorption of humic acids on the magnetic particle surface leads to an enhanced electrostatic and steric stabilization of particles, due to the absorbed layer of highly charged macromolecular compounds. The sorbents under study were found to reveal a high sorption capacity towards uranyl ions. Using the adsorption isotherm, in the linear form of the Langmuir equation, the adsorption parameters were estimated. The results obtained show that the adsorption of uranyl ions by the magneto-active nanocomposite is enhanced in comparison with the free HA.

Keywords: humic substances; magnetite; nanocomposite; uranyl ions

Introduction

HS are ubiquitous in the environment and comprise the most abundant pool of non-living organic matter. Their peculiar feature is polyfunctionality, which enables them to interact both with metal ions and organic chemicals.[1] The palette of interactions involves ion-exchange, complexation, redox transformations, hydrophobic bonding, etc. As a result, both chemical and physical speciation of the ecotoxicants, as well as their bioavailability, are impacted greatly by HS. This has been proven by numerous measurements on both bioaccumulation and toxicity of heavy metals and organic chemicals. In this context, application of humic-based products as sorbents can be of particular advantage. Sorbents are widely used as separation media in water purification to remove inorganic and organic pollutants from contaminated water. Recent research indicate that humic acids (HA) have high affinity to magnetic Fe_3O_4 nanoparticles, and sorption of humic acids (HA) on the Fe_3O_4 nanoparticles enhances the stability of nanodispersions by preventing their aggregation.[2] The treatment exploiting of coating Fe_3O_4 magnetic nanoparticles with humic acids can represent an environmentally friendly technology, since iron oxides (mainly magnetite) and HS are non-toxic. The prospects for practical application of HS as sorbents are determined by huge resources of humic materials accumulated in the form of lignites, peat, sapropel, composts, vermicomposts, and other humified biomass.

Here we report the formulation of efficient sorbents based on humic substances and magnetoactive nanoparticles. The resulting magneto-active composite

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nanomaterial, carrying sorbed contaminant (uranyl ions and heavy metals), is removed from mining water and transported by magnetic separation.

Experimental Part

Parent Humic Material

Humic materials used were isolated from oxidized brown coal of a Kyrgyzstan deposit. The isolation procedure included an alkaline (0.1 M NaOH) extraction as described elsewhere. The obtained alkaline extract was acidified to pH 2 using concentrated HCl. The precipitated HA were centrifuged, washed out with distilled water, dialysed, evaporated to dryness at 60 °C, and stored in a desiccator over P_2O_5.

Synthesis of Crystalline Hydrate $FeCl_2 \cdot 4H_2O$

To 10 mL of water and 17 mL of hydrochloric acid (density 1.19 g/mL) in china, 6.0 g of Fe powder was gradually added. The intense evolution of hydrogen was observed. After cooling the solution was filtered and evaporated. Then the filtrate was cooled, the blue crystals formed were filtered and dried in vacuum.

Preparation of Fe_3O_4 Magnetic Particles

The $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ salts (the aqueous solutions of 10 wt.% concentration) were mixed at $Fe^{3+}/Fe^{2+} = 2/1$ in inert atmosphere. Then NH_4OH (25 wt.%) was added with vigorous stirring. The dark precipitate was observed. The co-precipitated NH_4Cl was removed by repeated washing with hot distilled water. The solid product was placed in a desiccator over concentrated H_2SO_4 for two days under argon. The obtained product is magnetic.

Fe_3O_4 – humate composites were prepared by *i*) the *ex situ* method, which consists of the precipitation of magnetic particles followed by their incorporation into the HS matrix, *ii*) a chemical precipitation method *in situ* when the magnetic particles are grown within the HS matrix, and *iii*) the mechanochemical method, using the Fritsch Pulverisette grinder. In the preparation of Fe_3O_4 magnetic particles – HS nanocomposite by the coprecipitation method *in situ* some modifications were made: i) the use of room temperature in the precipitation, instead of a temperature of 60°C, ii) doubling of the amount of ammonium hydroxide added; iii) using the inert atmosphere (argon) in all stages.

Mechanochemical Synthesis of Magnet-active Nano-Hybrid Composite

In a typical procedure, 5 g of magnetite prepared according to the procedure, as described above, and 50 g of humic acid were placed into an agate mortar with agate balls and milled in a Fritsch Pulverisette grinder for 30 min (the volume is $4 \cdot 10^{-4}$ m^3, the rate is 1200 rpm). All the procedures were carried out in an inert atmosphere.

Sorption Behavior Humics-Based Sorbents Towards UO_2^{2+} and Heavy Metal Ions

Sets of adsorption experiments on the systems with either free (UO_2^{2+}/HA) or magnetite nanocomposite components (UO_2^{2+}/Fe_3O_4-HA) were carried out, the experimental protocol of these systems being identical. In a typical experiment, adsorption of UO_2^{2+} ions was conducted on a $UO_2(NO_3)_2$ solution in water with a concentration of $5.2 \cdot 10^{-5} - 6.6 \cdot 10^{-3}$ M. The uranium concentration in the supernatant was determined by using a concentration photocolorimeter "KFK-2" (λmax = 655 nm). Analysis were conducted in a high acidic medium (HNO_3, d – 1.4 g/mL) in the presence of arsenaso III.

Characterization of samples by transmission electron microscopy (TEM) was carried out by using a Hitachi H-7000 microscope. The structure of the materials, after all stages of preparation, was studied by X-ray diffraction (Philips X-pert, Cu-K_α). Mössbauer spectroscopy was done at 295 K, spectra were recorded on a spectrometer (WISSEL) with a Co^{57}(Rh) source in the constant acceleration regime. The calibration by rates was performed relative to the spectrum of metallic α-Fe.

Results and Discussion

Synthesis and Structure of Magnetic Nano-Hybrid Composites

It has been shown that the magnetic particles of iron oxides can be produced by *i*) the *ex situ* method of precipitation, *ii*) a chemical precipitation method *in situ,* and *iii*) a mechanochemical method. It is known that the aqueous coprecipitation method has some major drawbacks concerning to the control of the average size and monodispersity of the produced magnetite nanoparticles. The nature of the counterions and pH of the suspensions plays an important role in stabilizing the charged magnetic particles. Mossbauer studies have shown that chemical co-precipitation of Fe(II) and Fe(III) salts by addition of NH_4OH can be accompanied by the formation of iron oxyhydroxide that can be easily converted to Fe_2O_3. In the experiments, we observed that the product had a yellow-brownish color, an indication of the presence of the Fe_2O_3. Thus, the methods proposed were proven in their reproducibility and in the better control of the composition, size and morphology of the magnetic particles in the HS matrices.

According to X-ray diffractometry studies the major phase formed during a chemical coprecipitation in the presence of humic acid in situ is a magnetite Fe_3O_4 (Figure 1). The methods proposed provide an efficient way to control the shape and size distribution of nanoparticles and, unlike inorganic synthetic methods, do not require heating at high temperatures. The synthetic conditions – the excess amount of NH_4OH, the precipitation temperature (20–60° C), inert atmosphere, the large concentration of HS (1.5–2 mmol/g of magnetite) – ensure the formation of the stable Fe_3O_4 nanoparticles over γ-Fe_2O_3, which has a smaller magnetic susceptibility.

Analysis of the Mössbauer spectra recorded at 80 K evidences further the decrease of the amount of the phase containing Fe^{III} and the increase of the magnetite content. The values of hyperfine fields representing Fe_3O_4 in tetrahedral and octahedral sites are 51.2 T and 46.6 T, respectively. The hyperfine field representing the unidentified phase is 37 T. A monotonic decrease of the content of the phase containing Fe^{III}, from 65.47% to 13%, at 300 K and 80 K was observed respectively, accompanied by the increasing amount of magnetite suggesting the existence of superparamagnetic particles of magnetite.

Mechanochemical processing is a novel method for the production of nanosized materials.[3] The method has been widely applied to synthesize a variety of nanoparticles including ZnS, CdS, $LiMn_2O_4$, SiO_2, and CeO_2.[4–6] We have synthesized for the

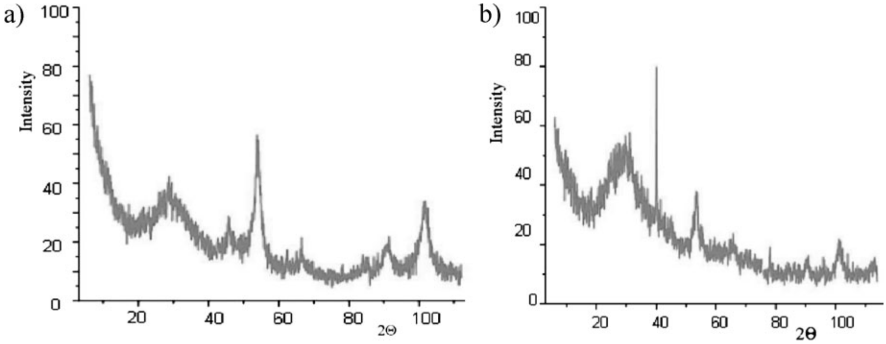

Figure 1.
XRD patterns of (a) the Fe_3O_4 nanoparticles-humic acids nanocomposite obtained by the chemical coprecipitation method *in situ* and (b) the Fe_3O_4 nanoparticles-humic acids nanocomposite obtained by the mechanochemical method.

first time the Fe_3O_4 nanoparticles and humic acid hybrid nanocomposite using the mechanochemical method. The advantage of such approach is that the mechanochemical technique is particularly suitable for mass production, because it is a simple and inexpensive process.

Transmission electronic microscopy studies of the humate-Fe_3O_4 nanocomposites obtained by a chemical coprecipitation in situ and by a mechanochemical synthesis showed that in both cases the fine nanoparticles, homogeneously distributed in the macromolecular matrix, are formed.

Figure 2 shows the TEM images of the hybrid nanocomposites obtained. Clearly the Fe_3O_4 nanoparticles are spherical and their diameters vary from 7 to 10 nm. No sharp distinction between the size and forms of the nanoparticles obtained by the different methods is observed.

Sorption Experiments

As shown from sorption experiments (see Figure 3), the sorbents under study are characterized by a high sorption capacity regarding to uranyl ions. Such a behavior can be caused by the formation of rather strong actinide complexes with humic acids. This is confirmed by the high value of their stability constants (logβ varies from 5.85 to 11 for complexes of the UO_2^{2+}- HA[7,8]). Using the adsorption isotherm in the linear form of the Langmuir equation form (the results were expressed as the ratio of the equilibrium concentration of uranyl ion to the adsorbed uranium amount $[UO_2^{2+}]_{eq}$/($[UO_2^{2+}]_{bonded}$ in g/L vs. the equilibrium concentration of uranyl ion ($[UO_2^{2+}]_{eq}$) in mmol/L the adsorption parameters can be estimated. Thus, for the system of UO_2^{2+}/HA K_{sorb} is equal to $(4.1 \pm 1.6) \cdot 10^4$ 1/M, Q_{max} is equal to 0.3 ± 0.05 mmol/g, in the

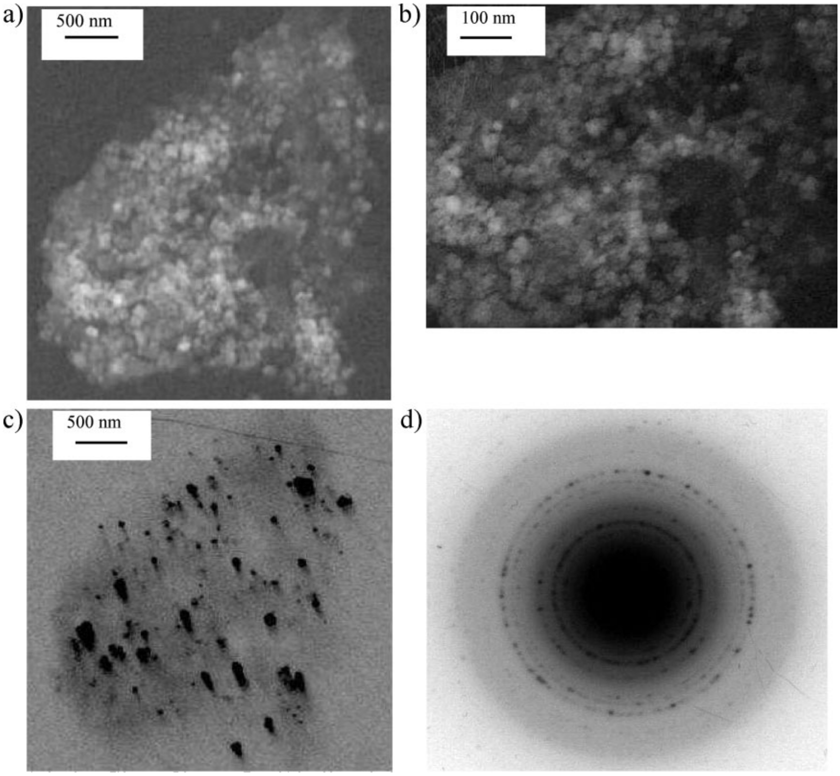

Figure 2.
TEM images of the humate – Fe_3O_4 hybrid nanocomposite obtained by a chemical precipitation: bright-field (a,b) and dark field images (c), and electron diffraction (d).

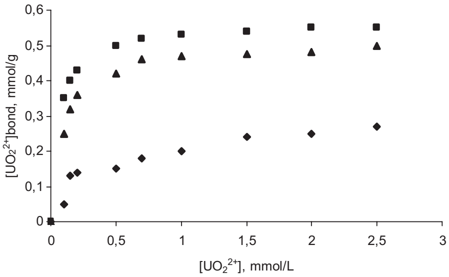

Figure 3.
The adsorption isotherms of UO_2^{2+} ions onto HA (◆); HA-Fe_3O_4 nanocomposite in the absence (■) and HA-Fe_3O_4 nanocomposite in the presence of Mg^{2+} ions (▲).

case of the UO_2^{2+}/HA-Fe_3O_4 K_{sorb} is equal to $(3.5 \pm 1.4) \cdot 10^4$ 1/M, Q_{max} is equal to 0.56 ± 0.02 mmol/g. The results obtained indicate that the adsorption of uranyl ions by the magneto-active nanocomposite is enhanced in comparison with the free HA. It is known that adsorption behavior of UO_2^{2+} ions by mineral oxides can be greatly changed depending on the experimental conditions (pH, ionic strength, the presence and absence of humic acids).[9,10] For the systems studied when the magnetite particles stabilized by macromolecules of HA form the stable colloid dispersion in the wide range of pH, the enhanced sorption capacity of the magnetite-HA nanocomposite can be accounted for by a high dispersion of nanoparticulated magnetite. The magneto-active sorbents synthesized reveal the same adsorption properties for heavy metals. Thus, for adsorption of Cd^{2+} ions by magneto-active nanocomposite the following parameters were estimated: $K_{sorb} = 760$ 1/M, $Q_{max} = 0.96$ mmol/g.

Alkaline and alkaline earth metal ions may influence the association of heavy metals with the humic material, since they are generally present in large excess over the heavy metals, since concentration levels of the former are found to be in the range $10^{-5} - 10^{-2}$ M. The speciation of heavy metals in HA solutions may be affected by the presence of other cations, such as calcium and magnesium. Study the sorption behavior of Fe_3O_4-HA nanocomposite synthesized for UO_2^{2+} in the presence of competition ions Mg^{2+} was shown in Figure 3, curve ▲. The adsorption capacities first increased with the initial metal-ion concentrations of UO_2^{2+} and then reached a plateau value at an initial concentration of 2.70 mM. The competitive adsorption studies showed that the Fe_3O_4-HA nanocomposites synthesized had good adsorption selectivity for UO_2^{2+} with the coexistence of Mg(II) ions. According to the results, when only UO_2^{2+} was found in the eluate, its adsorption was 81.5% from a 2.7 mM initial solution. However, when there was UO_2^{2+} with the binary systems of Mg(II) and the coexisting amounts were increased up to 100 times that of UO_2^{2+} (250 mM), it was 79.6%. It was concluded that there was no serious effect on the adsorption of UO_2^{2+} even when the concentration of the coexisting ions was about 100-fold. In light of these finding, in the presence of Mg(II) ions, the hybrid Fe_3O_4-HA nanocomposites synthesized have a great advantage for the selective adsorption of UO_2^{2+} ions.

Conclusion

Evidence that Fe_3O_4 nanoparticles, stabilized by humic substances (Fe_3O_4/HS nanocomposite), can efficiently remove radioactive metal ions U(IV) from contaminated water is presented. Being magnetic, the nanoparticles are readily separable using an external magnetic field, while the humic acid coating effectively stabilizes the particles against aggregation. The particles are chemically stable over the pH range 2 to 11, which is more than adequate for practical conditions.

Furthermore, the Fe_3O_4/HS loaded with sorbed heavy metals and uranium can be simply recovered from water with a magnetic separation, at low magnetic field gradients, which can hopefully reduce water treatment expenses.

Exploitation of Fe_3O_4/HS nanoparticles as sorbents for *in situ* technologies for contaminated water treatment meets all key application requirements, products are developed with the application of modern approaches of ‘‘green chemistry’’, that require the optimization of chemical process by the principle of minimal wastes and maximal safety as for the intermediates, as well as for the target products of the production.

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