

Investigation of Removal of U(VI) From Aqueous Solutions by Organo-Montmorillonite Supported Iron Nanoparticles

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Abstract – A new class of nanoscale zero-valent iron particles supported on natural montmorillonite and organo-montmorillonite were synthesized and the feasibility for the removal of U(VI) was examined through laboratory batch test. Batch experiments indicated that the reduction of both U(VI) was much greater with organo-montmorillonite supported iron nanoparticles reaching removal rate up to 98.5% respectively at the initial metal concentrations of 10 mg/L. The obtained data have given the opportunity to figure out the mechanisms of U(VI) removal which may thus promote the industrial application of nZVI technique in environmental remediation by changing the hydrophilic – hydrophobic properties of source systems.

Key words: organo-montmorillonite, zero-valent iron nanoparticles, contaminants, aquatic environment, absorption, remediation uranium, reduction, XRD, FTIR

I. Introduction

Iron nanoparticles are very effective for the removal of a wide range of contaminants, such as chlorinated organics, heavy metals and radionuclides, providing enormous flexibility for both in situ and ex situ applications. Nevertheless, a major obstacle for more effective remediation still remains, which involves tendency of reactive nanoparticles agglomerate with rapid sedimentation, causing limited mobility of the nanoparticles in an aquatic environment [1,2].

The usage of this composite as a supporting material is justified by the fact that clay minerals are abundant, environmental-friendly and much cheaper than activated carbon and technologies such as pump-and-treat, steam treatment, flushing with solvents and surfactants and attenuation via bio-and phytoremediation [3-5]. Moreover, montmorillonite is a kind of clay mineral with a layered structure, high surface area and strong adsorption characteristic.

Comparisons were made between both unsupported and supported iron nanoparticles in removal of different metallic ions. In this study, U(VI) were chosen as pollutants to assess the performance of iron nanoparticles supported by organo-montmorillonite. Research of contaminant removal demonstrated that the remediation mechanism varies depending on the contaminant of interest. A combination of surfactants and montmorillonite probably enhances the transport of iron nanoparticles through the contamination plume in the subsurface environment.

II. Experimental part and discussion

Materials and Methods

Montmorillonite was obtained from Cherkasy, Ukraine, trihydrosulfate uranium ($\text{UO}_2\text{SO}_4 \cdot \text{H}_2\text{O}$), ferrous chloride

tetrahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and hexadecyltrimethylammonium bromide (HDTMA) ($\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$, sodium borohydrate (NaBH_4) was purchased from (Merck, Germany). All presented chemicals were obtained in high purity and used as received. Montmorillonite had a cation exchange capacity (CEC) of 1 meq/g. [6].

The organo-montmorillonite was prepared due to dispersing 10 g of montmorillonite in 200 ml deionized water with ultrasound for 15 min. A solution of HDTMA 3.6445 g in 20 mL water was added under magnetic stirring. After 3 hours of reaction with stirring at 60 °C the final suspension was subjected to centrifugation followed by continual washing after which it was dried at 80 °C for 10 hours, and finally pulverized to pass through a 200- μm mesh sieve. The similar preparation method was reported previously [7].

To investigate the infrared spectra used KBr pellet method – 3 mg of the sample is well mixed into 300 mg fine alkali halide (KBr) was performed on Fourier spectrometer Spectrum-One FT-IR in the range 4000 – 4500 cm^{-1} where the sample was being subjected twenty consecutive times to scan with the resolution of 4 cm^{-1} .

The FTIR analysis was performed in an ultrasonic disperser UZDN – 2T.

X – ray analysis of initial and modified samples was conducted with the help of a diffractometer DRON – 4-07 in the range 1 – 60°(2 θ) with the usage of CuK α -radiation.

Removal processes of U(VI) from water were studied on standard test solutions, which were being prepared with distilled water and use of $\text{UO}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and 1M NaCl solution in order to obtain a desired ionic strength ($I = 0,01$). Ionometer I – I60M was used for standard test solutions. pH value adjustment with the use of NaOH and HCl solutions.

Experiments on removal U(VI) were carried out in static conditions at 25 °C temperature. Mineral sample in the experiments was 0.1 g, liquid phase volume – 50 cm^3 . After reaching adsorption equilibrium (within 1 hour) liquid phase was separated by centrifugation in which subsequently the equilibrium concentration of U(VI) was determined by spectrophotometry method Spectrophotometer UNICO 2100 UV, going by the standard methodology with the use of Arsenazo (III) reagent at wavelength of 670 nm.

Synthesis of zero-valent iron particles

Zero-valent iron particles (nZVI) were prepared by a liquid phase reduction method with borohydrate. This method is considered as the most common one due to its productivity and simplicity. The major part is to prepare the solution of FeSO_4 and NaBH_4 . In each batch, 12.4330 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 100 ml solution consisted of 80 ml H_2O and 20 ml absolute ethanol. It has been reported that the use of ethanol prevents oxidation of the particles during the preparation greatly [8]. Then amounts of 2 g montmorillonite (Mont) or : organo-montmorillonite (HDTMA-Mont) were dispersed in the FeSO_4 solution by magnetic stirring. 4.1635 g of NaBH_4

was dissolved in 110 ml of deionized water in order to obtain 1 M solution for preparation of NaBH₄ solution. Finally the NaBH₄ solution was added into montmorillonite – FeSO₄ dispersion. Synthetic sorbents title respectively Mont/nZVI and HDTMA-Mont/nZVI. (Fig. 1).

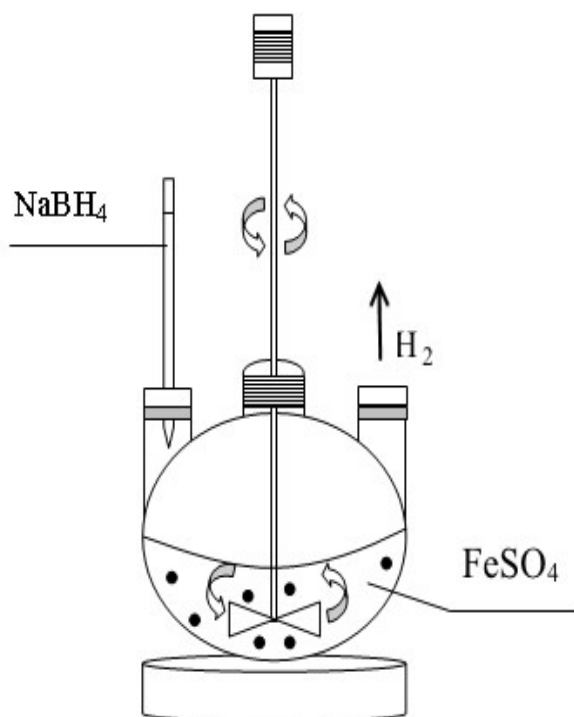


Fig. 1. Installation for the synthesis of nanomaterials

X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectra analysis

Two reflections are shown at 1° and 5° on XRD, the second of which associated with the (001) reflection of montmorillonite, the same as with Mont/iron and the first one is attributed to the large d-spacing, interpretation of which is unclear. It has been assumed that it is reflection of the existence of a highly correlated porous structure. Based on recent research in the structure of supported iron nanoparticles, the schematic representation of the sectional structure of the clay minerals supported iron nanoparticles was suggested [1]. The clay interlayer spaces accommodated the iron nanoparticles thus preventing them from aggregation. It was also suggested that the three-dimensional co-aggregation of clay platelets and iron hydroxyl cations or iron oxide nanoparticles caused the large d-spacing at 1° angle.

The indication of the zero-valent iron having been successfully supported on organo-montmorillonite is an obvious characteristic diffraction peak of Fe⁰ appearing at 2θ = 45° for both nZVI and Mont/iron on FTIR spectra [1–3]. The –CH₂– groups bands of the alkyl chains were weakened in the spectrum of HDTMA-Mont/nZVI. Presumably these shifts in the –CH₂– vibrational bands are due to the strong interactions between surfactant tails and the mineral surface [9]. Accordingly, there may be structural changes in that adsorbed surfactant molecules

change from the aggregated-cluster state (e.g., micelle-like state) to a more dispersed state lying on the surface, preferring an interaction with the mineral surface instead with alkyl groups at low surface coverage.

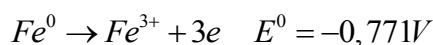
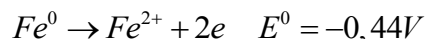
Removal performance of U(VI) analysis

According to the various references, the core-shell structure of the nanoparticles is responsible for great ability of nZVI to absorb metal ions from aqueous solution by multiple mechanisms, which are closely related to reduction and precipitation, electrostatic adsorption, complex formation. It has been reported that oxidation-reduction mechanism seems to be quite effective in the uptake of number of ions which have higher standard reduction potential than Fe²⁺. These include Ag⁺, Cu²⁺, Ni²⁺, Pb²⁺, Cr(VI), As(III) and As(V) [10].

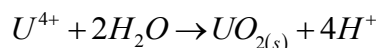
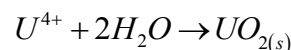
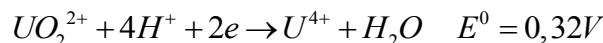
The mechanisms of U(VI) reduction by Fe⁰ are a cyclic and involve multiple reactions of electrochemical corrosion.

Removal of U(VI) takes place on the following mechanism. NNZ is a source of dissolved Fe(II), Fe(III), hydrogen, free radicals and other compounds, including iron hydroxo that can make a significant contribution to the removal of uranium.

Initially, the reaction Fe⁰ acts as a reducing agent, which further facilitates the removal of uranium. Interaction Fe⁰ and products of oxidation of Fe(II) and Fe(III) leads to the formation of adsorption centers.



The dissolution NNZ conditions for uranium deposition:



It should be noted that the transition U(VI) to U(IV) is a solution of particles near Fe⁰ resulting electrochemical reaction. As a result, the transition of uranium compounds in the solid state and deposition on the surface of iron. Also, the sorption complexes of U(VI) can form a solid mixture of U(IV) / U(VI) [11].

III. Results of investigation X-ray diffraction (XRD)

The basal spacing of Mont was 1,24 nm, which is common for Na-montmorillonite. The basal spacing enlarged up to after the reaction with hexadecyltrimethylammonium ions [1]. The XRD diffractogram of the synthesized nZVI particle has characteristic 2θ value of 45°, and signal for iron oxides with a 2θ value of 32° and 35° were found (Fig. 2). These diffraction patterns along with the calculation of the Scherrer equation proved that the iron is mainly in its zero-valent state.

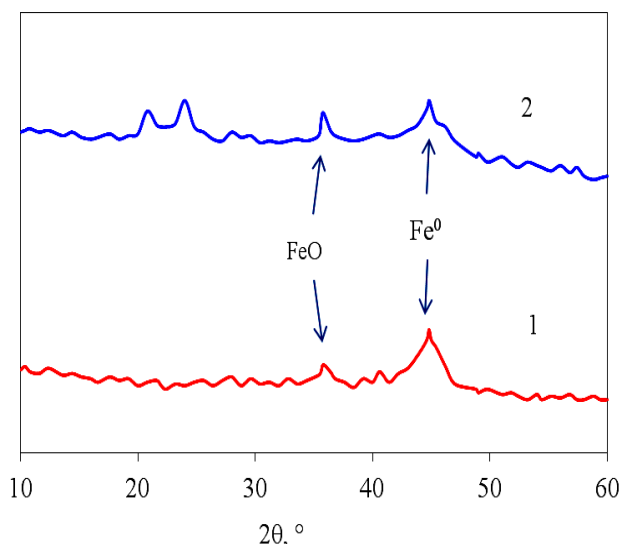


Fig. 2. X-ray diffraction patterns of: 1 - supported iron nanoparticles (HDTMA-Mont/nZVI, 2 - iron nanoparticles

Fourier Transform Infrared (FTIR) spectra

For HDTMA-Mont, bands at 2920 and 2850 cm^{-1} were due to groups of the alkyl chains.

In the IR spectrum of the iron-montmorillonite (OMMT/NNZ) observed weakening bands $-\text{CH}_2-$ groups alkyl chains at 2920 and 2850 cm^{-1} . New band is also appeared in the spectra of these samples at 625 cm^{-1} , which is characteristic for stretching fluctuations Fe-O (Fig. 3).

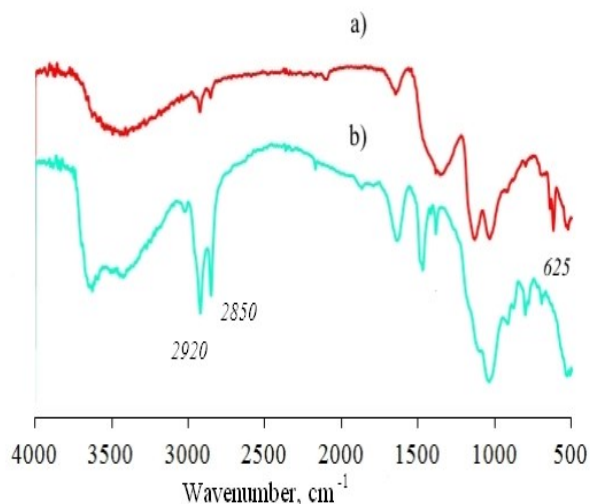


Fig. 3. FTIR spectra: a – supported iron nanoparticles (HDTMA-Mont/nZVI); b – organic montmorillonite (HDTMA-Mont)

Reduction performance with U(VI)

As shown on figures, the reduction of U(VI) reduction the following tendency can be observed: HDTMA-Mont/nZVI > Mont/nZVI > nZVI > HDTM-Mont > Powdered iron > Mont (Fig. 4).

Montmorillonite has a net negative structural charge due to isomorphous substitution of cations in the crystal

lattice [12]. On account of this negative charge, Mont has little or no affinity for anionic species.

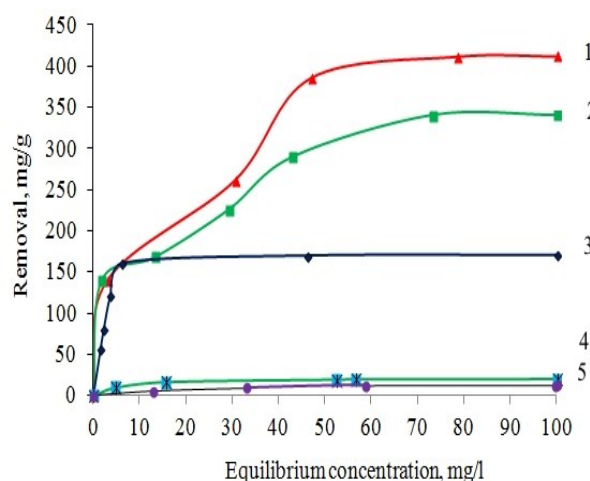


Fig. 4. Removal rate of U(VI) as a function of Equilibrium concentration (1 – HDTMA-Mont/nZVI, 2 – Mont/nZVI, 3 – nZVI, 4 – HDTMA-Mont, 5 – Mont)

However, modifying clay mineral surfaces with surfactants converts the hydrophilic silicate surface to the positively charged hydrophobic one. Thereby, HDTMA-Mont reveals more reactivity towards the U(VI) removal compared to unmodified Mont, reaching adsorption values of 98,5 % at initial U(VI) concentration equals 10 mg/L .

Effect of pH on metals removal

The effect of pH was determined by examining removal U(VI) at the following constant factors: Temperature = 25°C, agitation speed = 250 rpm, U concentration = 50 mg L^{-1} , nanocomposite dosage – 0.1 g L^{-1} , contact time = 60 minutes. In connection with the high resolution obtained sorbent to extract ions U (VI) from aqueous solutions was decided to put the experiment in terms of uranium ions concentration of 50 mg / L . Due to the high ability to removal of ions of U (VI) from aqueous solutions, it was decided to put the experiment at the these conditions.

For U (VI) sorption dependence on the pH of the complex, which is associated with the ability of uranium to form complexes at different pH values.

At pH close to neutral and under contact with air, corresponding to surface waters, the dominant form of U (VI) in solution are uranyl ion UO_2^{2+} and its hydroxo UO_2OH^+ , $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_4(\text{OH})_7^+$ and others [13].

As can be seen from the data presented in Fig. 5, the curves of sorption of uranium are typical of layered silicates (Mont domed shape with a maximum at neutral pH, when there is a dissociation of surface groups [14], which is typical for Mont/nZVI. At low pH when the dissociation of surface groups suppressed and, at high pH values when the prevailing forms of uranium in solution are neutral or even negative forms, sorption decreases. At the same time, the modified mineral samples are substantial differences in the nature of sorption curves.

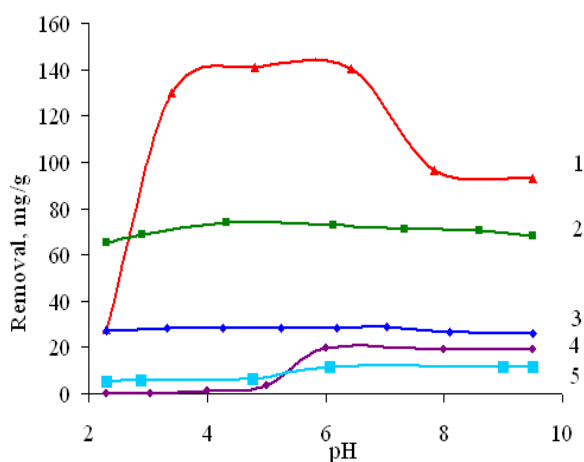


Fig. 5. Removal rate of U(VI) as a function of pH (1 – HDTMA-Mont/nZVI, 2 – Mont/nZVI, 3 – nZVI, 4 – HDTMA-Mont, 5 – Mont).

With increasing pH with increasing concentration in solution anionic form of uranium sorption value decreases much more slowly, due to the formation on the surface is double layer and its recharge HDTMA. For sample HDTMA-Mont/nZVI observed typical domed shape curve at low and neutral pH values and higher values of sorption on pH equal to 7 and a slight decrease in sorption at high pH, due to partial compensation charge on the surface HDTMA-Mont/nZVI.

Conclusions

Nanocomposite supported iron nanoparticles appeared to be more effective in terms of the removal of U(VI) than unsupported iron nanoparticles.

The use of organo-montmorillonite could greatly enhance the reduction activity of nanoscale zero-valent iron due to its capability to prevent their aggregation.

Nanocomposite showed an outstanding ability to remove metal ions because of high surface activity and low particle size. After the contact with U(VI), the reduction of those was highest with HDTMA-Mont/nZVI, followed by Mont/nZVI and unsupported nanoparticles, what may thus offer an economically and environmentally friendly usage of organoclay nanocomposite as an exceptional solution to one of the most aggravating ecological problems.

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