Applicability of Ferromagnetic Nanoparticles in the Retention of Heavy Metals from Aqueous Solutions

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In this paper are presented the experimental results obtained in the study of applicability of ferromagnetic nanoparticles in the retention of heavy metals from aqueous solutions. The influence of magnetic nanoparticles based on iron, cobalt and nickel on turbidity, pH, permanganate index, aluminum, copper, cadmium and lead was studied. The study shows that conventional water treatment systems combined with acrylic polymer can be improved by adding magnetic nanoparticles. Experimental data has shown that the presence of magnetic nanoparticles based on iron, cobalt and/or nickel increases the efficiency of the treatment system and is reflected by all analyzed parameters.

Keywords: ferromagnetic nanoparticles, aluminum, copper, cadmium, lead

Access to drinking water is the key to protecting public health; clean water has become a basic need for all companies operating properly [1]. Despite their presence in low concentrations, environmental pollutants present serious threats to supply drinking water, living organisms and public health [2].

Heavy metals are pollutants that are not biodegradable and are very difficult to remove naturally from the environment. Almost all elements of heavy metals are extremely toxic, when their concentration exceeds their permissible limit within the ecosystem. Large concentrations of heavy metals can accumulate in the human body once they enter the human food chain and cause serious health problems when metals exceed the permissible concentration [3-6].

Contamination of water with toxic metal ions (Hg (II), Pb (II), Cr (III), Cr (VI), Ni (II), Cu (II)), As (V) and As (III)) becomes a public environmental issue and severe health. Various techniques such as: adsorption, precipitation, ion exchange, reverse osmosis, electrochemical treatments, membrane processes, evaporation, flotation and oxidation are used to remove heavy metals [7- 9]. Of these, adsorption is a conventional technique, but effective to remove toxic metal ions and pathogens from water.

The synthesis of magnetic nanoparticles has been extensively developed not only for fundamental scientific interest but also for many technological applications such as: magnetic resonance imaging, ferrofluids for audio speakers and magnetic recording media [10]. In particular, the use of magnetic nanoparticles as adsorbents in water treatment offers a convenient approach to separating and removing contaminants by applying external magnetic fields.

The magnetic nanoparticles are sensitive to air oxidation and are easily aggregated in aqueous systems [11]. Thus, for the application of these nanoparticles in various potential fields it is advisable to stabilize the iron oxide particles by surface modification. The magnetic structure of the surface layer which is usually very different from the nanoparticle center may have a notable effect on the magnetic properties of the nanoparticles and composites [12]. Size control and poly-dispersion are also very important, because nano-crystalline properties depend on nanoparticle size. It is interesting to note that only magnetic particles with a size smaller than 30 nm have large surface area and have super-paramagnetic properties that make them prone to magnetic fields and do not become permanently magnetized without an external magnetic field to support them [13]. These properties are extremely useful in developing new separation processes [14].

This paper is based on the previous experience of the research group on the preparation and characterization of magnetic nanoparticles [15-20] and their use in order to regulate the biological load of the water [21], now approaching the removal of metal ions of interest.

Experimental

Reagents and apparatus

Nitric acid (HNO_3, p = 1.4 g/mL) was purchased from Fluka, while the standard copper solution of 1000 mg/L Cu ($Cu(NO_3)_3$ in 0.5 mol/L HNO_3), the standard cadmium solution of 1000 mg/L Cd ($Cd(NO_3)_2$ in 0.5 mol/L HNO_3) and the standard lead solution of 1000 mg/L Pb ($Pb(NO_3)_2$ in 0.5 mol/L HNO_3) were purchased from Merck. Nitric acid of 0.03 mol/L was prepared by diluting the concentrated nitric acid (p = 1.4 g/mL). Aluminum sulfate and sodium acrylate were purchased from Merck. Reagents were prepared with distilled water.

The magnetic nanoparticles were previously obtained and presented in the our group [15-18, 20-22].

The used tested systems for the sample water treatment were presented in table 1.

Procedures and Analytical Methods

For the experiments, each type of nanoparticle was mixed and the heavy metals solutions of known concentrations were prepared. Subsequently, they were directly contacted in 500 mL containers for 20 days with continuous stirring at a rate of 45 rpm. The samples for physical-chemical analysis and atomic absorption were sampled. For samples with coated nanoparticles several extractions with chloroform before atomic absorption were performed (to remove the traces of undecylenic acid).

Analytical control was performed using an atomic absorption spectrophotometer AAnalyst 800 (Perkin Elmer instruments - USA) at a wavelength of 324 nm for copper, 229 nm for cadmium and 284 nm for lead, an AN 2100 turbidimeter for turbidity determination, a pH meter WTW

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Table 1
BASED CHARACTERISTICS OF THE USED SYSTEMS

Used systems	Symbol	Medium diameter (nm) [15,22]	Covering layer
Havy Metals Solution	HMS	-	-
Alumminium Sulfate	AS	-	-OH
Acrylic Polymer	P	-	-COOH
Fe(III)/Fe(II) Nanoparticles	Fe(III)/Fe(II) NP	20	-OH
Fe(III)/Fe(II) Coated Nanoparticles	Fe(III)/Fe(II) CNP	15	-C-....-C=CH_2
Fe(III)/Ni(II) Nanoparticles	Fe(III)/Ni(II) NP	30	-OH
Fe(III)/Fe(II) Coated Nanoparticles	Fe(III)/Ni (II) CNP	25	-C-....-C=CH_2
Fe(III)/Ni(II) Nanoparticles	Fe(III)/Co(II) NP	35	-OH
Fe(III)/Fe(II) Coated Nanoparticles	Fe(III)/Co(II) CNP	30	-C-....-C=CH_2

for *p*H determination; a DR 6000 spectrophotometer for aluminum determination. The permanganate index was determined by a volumetric method.

After adsorption the retention of the species of interest (**R**) was determined using the solutions' absorbance and concentration [23-27]:

$$R = (c_o - c_f)/c_o \qquad (1)$$

where c_f - the final concentration of the solute (metalic ions),

c_o – the initial concentration of solute (metalic ions)

$$R = (A_o - A_{sample})/A_o \qquad (2)$$

where:

A_0- initial sample solutions absorbance

A_{sample}- current sample absorbance

Results and discussions

Improvement of classical water treatment systems with aluminum sulfate and/or acrylic polymers is a current objective, especially as the residual presence of aluminum in treated waters represents a potential health and environmental hazard has been shown [1-4].

In the present case, the efficiency of the ferromagnetic nanoparticles complementary to the classical treatment system was achieved by measuring physico-chemical parameters at the end of the experiments: turbidity, *p*H, permanganate index, and aluminum, cadmium, copper and lead at the end of the experiments.

The influence of previously obtained magnetic nanoparticles [12 – 16] Fe (II)/Fe (III) magnetic nanoparticles, coated Fe (II)/Fe (III) magnetic nanoparticles, Fe (III)/Ni (II) magnetic nanoparticles, Fe (III)/Co (II) magnetic nanoparticles, coated Fe (III)/Co (II) magnetic nanoparticles on turbidity, pH, permanganate index, aluminum, cadmium, copper and lead was studied.

The working conditions were: 30 mg/L aluminum sulfate (AS) dose, 0.06 mg/L (P) polymer dose, 5 mg/L heavy metals solutions (HMS) and ferromagnetic nanoparticle dose.

Influence of ferromagnetic nanoparticles on turbidity

Turbidity is an important parameter in water quality monitoring by providing information both on the presence of organic and biological suspensions as well as metallic anions.

Experimental data showed that after 20 days using aluminum sulfate and polymer, maximum separation efficiency was recorded. Regarding the efficiency of magnetic nanoparticles on turbidity, the Fe (III)/Co (II) magnetic nanoparticles have the highest efficiency (fig. 1).

Of course, in all cases, the turbidity of aqueous solutions falls below the standard limits even for drinking water, but should be noted that when using nanoparticles the turbidity is higher, and in the particular case of tests with magnetic nanoparticles based on Fe (II)/Fe (III) turbidity is approaching the maximum admissible limit.

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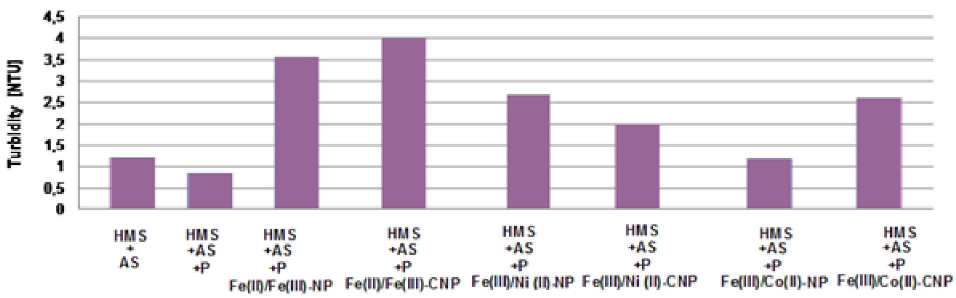

Fig. 1. Influence of ferromagnetic nanoparticles on treated water turbidity

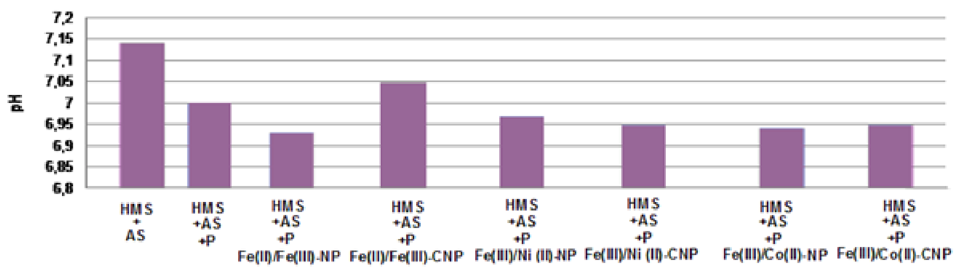

Fig. 2. Influence of ferromagnetic nanoparticles on treated water *p*H

Influence of ferromagnetic nanoparticles on pH

In addition to turbidity, the pH of the aqueous solution subjected to the experiment has been constantly monitored as water quality, but also as a potential operational parameter.

Experiments have been carried out on the influence of the ferromagnetic nanoparticle type on the *p*H, and the measurements made show a small variation of the *p*H between 6.9 and 7.2. Figure 2 shows the pH values for all systems tested after 20 days.

Experiments results have demonstrated that maximum efficiency has been recorded for Fe (II)/Fe (III) magnetic nanoparticles and the lowest efficiency has been reported for coated Fe (II)/Fe (III) magnetic nanoparticles.

Influence of ferromagnetic nanoparticles on permanganate index

Organic and inorganic reducing substances or microorganisms are well documented by the permanganate index.

Experiments were carried out on the influence of the type of ferromagnetic nanoparticles on the permanganate index after the same 20-day contact time (fig. 3).

Experiments using aluminum sulfate, polymer and coated Fe (II)/Fe (III), Fe (II)/Fe (III), Fe (III)/Ni (II) ferromagnetic nanoparticles were carried out. The best results were obtained for Fe (II)/Fe (III) nanoparticles and Fe (III)/Co (II) nanoparticles.

The coated Fe (II)/Fe (III) nanoparticles presented the lowest efficacy.

Influence of ferromagnetic nanoparticles on aluminium contains of the treated water

Aluminum is generally present in water treated with aluminum sulfate, but it is also a quality indicator that is generally taken into account because can be potentially toxic [1,4].

The experiments regarding the influence of the ferromagnetic nanoparticle type on the aluminum content after a previously agreed interval of 20 days been carried out (fig. 4)

Regarding the efficiency of ferromagnetic nanoparticles in aluminum ion retention was observed that the best results were recorded for the Fe (III)/Co (II) nanoparticles, being just below the classical treatments while the lowest results were recorded for Fe (III)/Ni (II) nanoparticles.

In the other hands can be argued that the practical use of ferro-ferrous nanoparticles would be beneficial and complementary to treatments with aluminum sulfate and/ or acrylic polymers.

Influence of ferromagnetic nanoparticles on cadmium contains of the treated water

Heavy metals with a negative impact on the environment and the toxicity of cadmium are representative and can be used as a tracer and quality index, especially when discussing industrial apiary effluents.

The experiments regarding the influence of the ferromagnetic nanoparticle type on the cadmium content after a previously agreed interval of 20 days been carried out (fig. 5)

The results of the tests showed that the retention of cadmium ions is achieved in small proportions compared to the initial solution (below 10%). The data, however, has shown that retention is more effective in the use of coated Fe (III)/Ni (II) nanoparticles (almost 10%) compared to Fe (II)/Fe (III) nanoparticles (below 5%).

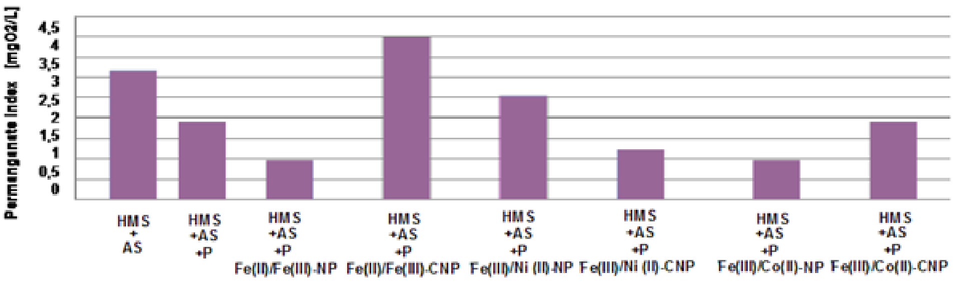

Fig. 3. Influence of ferromagnetic nanoparticles on permanganate index of the treated water

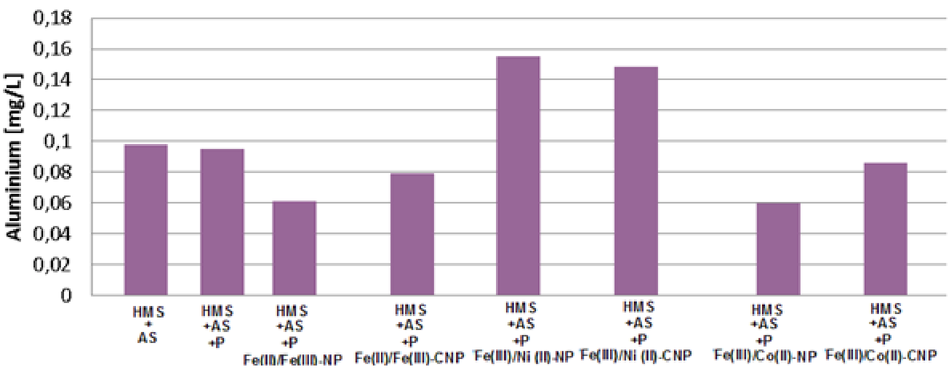

Fig. 4. Influence of ferromagnetic nanoparticles on aluminum of the treated water

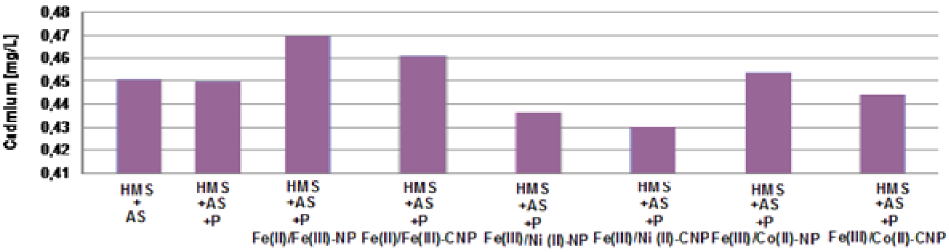

Fig. 5. Influence of ferromagnetic nanoparticles on cadmium contains of the treated water

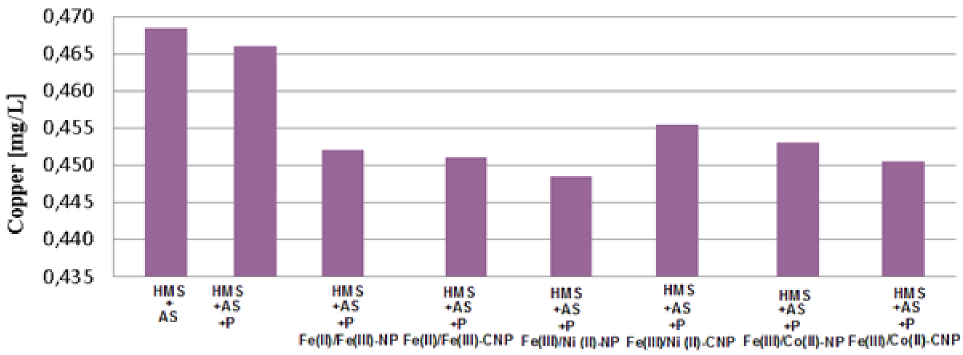

Fig. 6. Influence of ferromagnetic nanoparticles on copper contains of the treated water

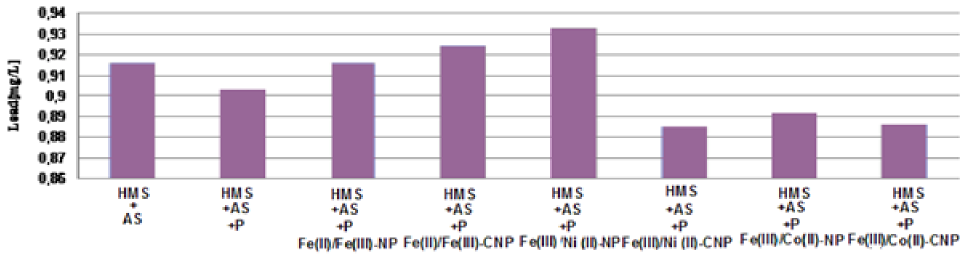

Fig. 7. Influence of ferromagnetic nanoparticles on lead contains of the treated water

Influence of ferromagnetic nanoparticles on copper contains of the treated water

Using aqueous solutions of similar concentrations to cadmium, the performance of the copper ion retention systems was tested.

Regarding the retention of copper ions, it has been found that the retention percentage is low.

The results regarding the influence of the type of ferromagnetic nanoparticles on the copper content after 20 days (fig.6) are inferior to the case of cadmium ions (fig.5), being generally much less than 10%.

By comparing the obtained results, a higher efficiency is obtained in this case also in the use of Fe (III) / Ni (II) nanoparticles.

It should be noted, however, that the effect of magnetic nanoparticles is positive, improving in all cases copper retaining compared to classic treatment with aluminum sulfate or aluminum sulfate and acrylic polymer.

Influence of ferromagnetic nanoparticles on lead contains of the treated water

In order to complete the heavy metal ion group of toxicological and environmental interest, experiments were conducted on the influence of the ferromagnetic nanoparticle type on the lead content of aqueous solutions after the same time interval (20 days), but using a double initial concentration compared to cadmium and copper (fig. 7).

Although initial conditions are less favorable, lead retention is significantly higher in all cases than cadmium cations, especially copper, with a value between 10 and 15%.

It is noted that the coated nanoparticles of Fe (III)/Ni (II) have a higher efficiency compared to other types of nanoparticles and treatment systems.

Conclusions

The study shows that conventional water treatment systems with aluminum sulfate and aluminum sulfate combined with acrylic polymer can be improved by adding magnetic nanoparticles.

Experimental data has shown that the magnetic nanoparticles based on iron, cobalt and/or nickel increases the efficiency of the treatment system and is reflected by all analyzed parameters: turbidity, *p*H, permanganate index, aluminum, cadmium, copper and lead.

Regarding the influence of the nanoparticle type on the turbidity it was found that the best results were obtained using the Fe (III)/Co (II) magnetic nanoparticles, while for the high pH the Fe (II)/Fe (III) nanoparticles and coated Fe (III) / Co (II) nanoparticles.

The Fe (II)/Fe (III) nanoparticles and the Fe (III)/Co (II) nanoparticles had a positive influence on the permanganate index.

For the retention of metal ions (Al^{3+}, Cd^{2+}, Cu^{2+}, Pb^{2+}), the percentage of this is still small (below 20 %), but comparing the results obtained for each type of nanoparticles, it was found that coated Fe (III)/Ni (II) nanoparticles for cadmium and lead and Fe (III)/Ni (II) nanoparticles for copper.

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