Applicability of Ferromagnetic Nanoparticles in Surface Water Treatment with Biological Loads

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This study was conducted in order to applicability of magnetic nanoparticles in order to reduce bio burdened surface water for drinking purposes. Ferromagnetic nanoparticles were obtained by co-precipitation method Cold salts based on iron, cobalt and nickel in strong basic medium. These magnetic nanoparticles have been used in various experiments which was intended to reduce the biomass content of a surface water potable purposes. Efficient use of nanoparticles in the treatment process was checked by spectrophotometric analysis, titration and microscopic analysis.

Keywords: magnetic nanoparticles algae blue green edging, surface water, settled water

Magnetic nanoparticles attracted scientific and technological interest because of the many advantages, among which chemical optical, magnetic and electrical properties. The magnetic nature of these nanoparticles depends on their magnetic stability, shape, purity and size. Final performances of the devices will be influenced by the characteristics of nanoparticles, namely: structure, size, shape and purity [1-2].

Nanoparticles can be synthesized by conventional techniques such as evaporation condensation processes, sol-gel processes, combustion methods, hydrothermal processes, pyrolysis techniques, micro emulsion techniques, electrochemical synthesis with patterned assisted method, wet chemical method, metal vapors, *sono*, named chemical reduction, condensing gas and co-precipitation process [1, 3-10].

Researchers have shown that Fe-Co-Ni nanoparticles can be successfully synthesized by *poliol* named method. Fe,Co,Ni based nanoparticles with micrometric dimensions were obtained by this method adding reducing bulking agent. FTIR analysis showed that carbonyl group from the oleic acid structure strongly coordinates the surface of the nanoparticles and SEM studies have confirmed the structure of the synthesized sample [11].

The magnetic nanoparticles are used in various fields of science and technology including: electronic photography, recording materials, catalysis, sensors, ceramic materials, medical industry, water treatment, biology, chemical industry, organic and inorganic pollutants, analytical applications, Magnetic Resonance Imaging [1, 10, 12].

Blue green algaes (phylum Cianophita) - play an important role in freshwater ecosystems and are less present in marine aquatic ecosystems. They are distinguished by a high adaptability to extreme variations of nutrients and environmental factors.

They frequently bloom in eutrophic basins; the highest development of Microcystis sp populations is seen in late summer. These types of algae are problematic in the surface water for drinking purposes treatment due to the presence of gaseous vacuoles which gives them buoyancy, allowing them to develop the population density vertically in the water, depending on conditions.

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Most of the cyanophytes have toxins in their composition (sp Aphanizomenon, sp Anabaena, sp Microcystis, sp Oscillatoria, sp Nostoc.). Because of the pollution of surface waters with nutrients in recent years, a blue-green algae overgrowth was observed.

Given that most people of the world population uses surface water as a water source, is important to identify the presence of these algae due to the effects the toxin has on the human body (liver dysfunction, or as inhibitors of serine / threonine protein phosphatase becoming promoters for different types of tumors).

The World Health Organization (WHO) has set a maximum limit allowed -LR alert microcystin 1.0 ppb (mg / L) in drinking water [13].

Microcystis is part of the *microcystinese* family, togetherwith other species of blue-green algae, including: Aphanocapsa, Phormidium, Anabaenopsis, Synechocystis Aphanocapsa, Arthrospira, Fischerella, Hapalosiphon, Planktothrix, Radiocystis, Cylindrospermopsis, Leptolyngbya, Synechococcus, Lyngby, Limnothrix, Woronichinia [14].

Microcystis site prevail in surface waters, slow, warm and cloudy waters. It produces a toxin called *microcystin* which has adverse effects for humans and animals when inhaled and ingested, such as: nausea, vomiting, diarrhea, fever, headache, pneumonia, liver injuries and dysfunctions. The main exposure sources are consumption of drinking water, food supplements and recreational exposure [15, 16].

This study shows the synthesis of magnetic nano-particles cold co-precipitation method and the performance evaluation of the effectiveness in terms of reducing the content of biomass in surface waters.

Experiemntal part

Materials, procedures and methods

Reagents

All reagents have analytical grade and were used without further purification.

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_3O$) nitrate, cobalt hexahydrate ($Co(NO_3)_2 \cdot 6H_3O$), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), iron sulfate and ammonium hexahydrate ($Fe(SO_4)_2(NH_4)_2 \cdot 6H_2O$), sodium hydroxide

(NaOH) were bought from Fluka, and ammonium hydroxide (NH_4), nitric acid (HNO_3), undecylenic acid ($C_{11}H_{20}O_2$) and ethanol (C2H6O) were purchased from Merck .

In the preparation of magnetic nanoparticles following reagents were used:

- preparations nanoparticles: Fe (III) / Fe (II): Ferric chloride hexahydrate, iron and ammonium sulfate hexahydrate and sodium hydroxide;

- preparing nanoparticles: Fe (III) / Co (II): hydrated cobalt nitrate, ferric chloride and sodium hydroxide;

- preparation of the nanoparticles Fe (III) / Ni (II) nickel nitrate hexahydrate, ferric chloride hexahydrate, iron sulfate hexahydrate and ammonium and ammonia.

Ethanol was used as solvent and undecylenic acid was used for coating the obtained nanoparticles.

All reagents were prepared with distilled water c = 1.02μs / cm.

Equipment

Glassware: 500 mL Erlenmeyer glasses 1000 mL beaker 250, 500 and 1000 mL, 100 and 500 mL cylinder, pipette 10, 25 and 50 mL.

Experiments were performed using the following laboratory equipment:

- machine type flocculator VELP Scientifica JLT6;
- 2100 AN Turbidimeter;
- WTW pH meter;
- multiparameter with conductivity depending on HACH;
- colloid mill type Retsch PM 100.

Procedure

The synthesis of magnetic nanoparticles such as Fe (III) / Fe (II), Fe (III) / Co (II), Fe (III) / Ni (II)

The magnetic nanoparticles of the type Fe (III) / Fe (II), Fe (III) / Co (II), Fe (III) / Ni (II) were synthesized by co-precipitation in the cold method, in strong alkaline medium [17-21].

For all three cases of obtaining magnetic nanoparticles, we did the same, so we added specific solutions for each nanoparticles target type [iron sulfate and ammonium hexahydrate 2M-for nanoparticles Fe (III) / Fe (II) solution of 2 M cobalt nitrate hexahydrate, the nanoparticles Fe (III) / Co (II) and nickel zotat nanopoarticulele 2M-to Fe (III) / Ni (II)] to a solution of ferric chloride hexahydrate 1M.

Over the above obtained solution were slowly added, with continuous stirring 15 g of sodium hydroxide each until *p*H ~ 12, this being maintained constant by continuous adjustment with sodium hydroxide.

We finally obtained a black precipitate, which is separated magnetically and subjected to the process of dialysis with the use of dialysis bags, up to pH ~ 11, parameter that is continuously kept under control.

After dialyzing, the nanoparticles were washed with distilled water.

Some of nanoparticles thus obtained were used in Jar-Test tests type and some were placed in the colloidal mill for 7 days, to begrounded, after adding 5 ml undecylenic acid, in order to make the nanoparticles functional and 20 ml ethanol and 50-60 g glass pearls. After taking it out of the colloid mill, functionalized nanoparticles (with undecylenic acid) were used in Jar-Test test type.

Preparation of working solutions used for conducting JAR - TEST type experiments

We prepared a series of solutions of aluminum sulfate (10%), aluminum sulfate nanoparticles type Fe (III) / Fe (II) (9.9% + 0.1%), aluminum sulfate nanoparticles of the type Fe (III) / Co (II) (9.9% + 0.1%), aluminum sulfate nanoparticles of the type Fe (III) / Ni (II) (9.9% + 0.1%), PAX, PAX nanoparticles type Fe (III) / Fe (II), PAX (polyvinyl aluminum) with type nanoparticles Fe (III) / Co (II) and type PAX nanoparticles Fe (III) / Ni (II). These solutions were used as coagulation solutions for conducting experiments Jar-Test type.

Jar-Test type experiments steps are presented below:

- In aseries 1000 mL beakers it is introduced with the help of a 1000 ml raw water graduated cylinder and we start stirring,

- in each beaker solution of the same concentration of coagulation was added using a pipette in various quantities;

- after the addition of the coagulation solution, we stirred continuously for 2 min at a speed of 160 rev / min;

- then stirring was continued for 15 min at a speed of 45 rev / min;

- we stopped the stirring and let the solutions settle for 15 min, followed by carrying out physicochemical and biological analyzes.

Results and discussions

Blue green algae (phylum Cianophita) – which plays an important role in freshwater ecosystems, are less present in marine aquatic ecosystems. It is distinguished by a high adaptability to extreme variations of nutrients and environmental factors. Production frequent blooms in eutrophic basins; Maximum development of Microcystis sp populations is seen in late summer (table 1). These types of algae are problematic in the treatment of surface water for drinking purposes because these vacuoles gaseous gives them buoyancy, allowing them to develop the density population vertically in the water, depending

Table 1
THE VALUE DETERMINED FOR TURBIDITY AND *p*H OF SURFACE WATER (RIVER) WERE MADE BY AVERAGING THE VALUES OF THIS PARAMETER IN JULY, AUGUST AND SEPTEMBER OF THE YEARS 2014 TO 2015

Year	Turbidity [NTU]*	pH *	phytoplankton and zooplankton [org/L]	% blue algae [org/L]	Aluminium sulfate dose [mg/L]	Aluminium polycloride dose [mg/L]
2014	1316	8.14	960.000	25	55	25
2015	569	8.43	15.000.000	98	80	40

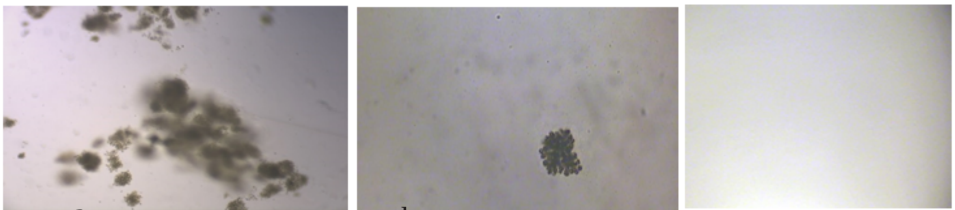
a b c

Fig. 1. Images micrographs of MCX 500 blue algae (Microcystis) in: *a) Raw Water (River); b) Setted Water; c) Chlorinated Water*

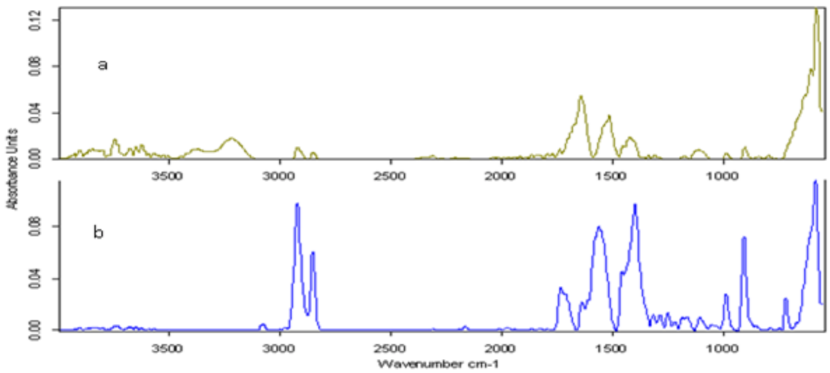

Fig. 2. FTIR spectra of magnetic nanoparticles of Fe (III) / Fe (II) not covered (a) and Fe (III) / Fe (II) covered (b)

on conditions (temperature, *p*H). Monitoring the proportion of blue algae in water surface during 2014-2015 showed its increase in development and is of a great importance due to the lack of cyclicality.

Analysis of magnetic nanoparticles of Fe (III) / Fe (II), Fe (III) / Co (II) and Fe (III) / Ni (II)

After synthesis, magnetic nanoparticles were analyzed using a Bruker FTIR with Tensor 27 (figs. 2 and 3). In the spectrum of figure 2 (a) we observe specific bands hydroxyl group at 3000-3500 cm^{-1}, which demonstrates that nanoparticles coated summary shows a shell-type hidroxocomplex, there are hydrogen bonds (H). Regarding spectrum analysis in figure 2 (b) we notice the decrease of specific bands hydroxyl group, intensifying specific bands in the range 2800-3000 cm alkyl and COOH range -1800 - 1700 cm^{-1}, which shows that undecylenic acid for these nanoparticles made a good functionalization.

The spectrum of figure 3 (a) specific bands indicates the presence of hydroxyl groups at 3100 cm^{-1} to 3700 cm^{-1} and it is noticeable to further increase the range 3100 - 3500 cm 1. After coating, the disappearance of the bands is observed specifically the groups hydroxy, increasing and expanding link C = O at 800 cm^{-1} to 1200 cm^{-1} and the appearance of specific bands alkyl group 2800 cm-1 to 3000 cm^{-1}.

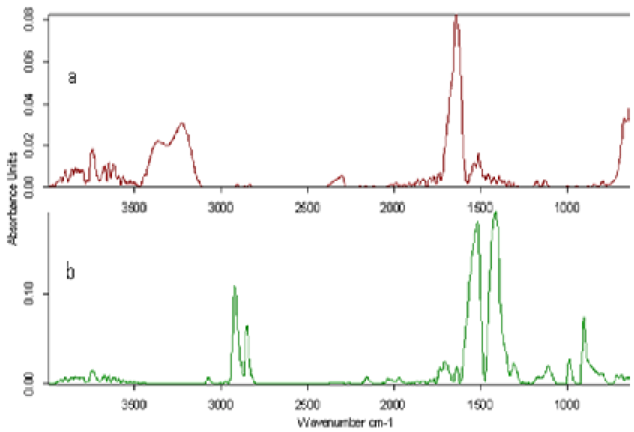

Fig. 3. FTIR spectra of magnetic nanoparticles of Fe (III) / Co (II) not covered (a) and Fe (III) / Co (II) covered (b)

Following the comparative analysis of spectra of magnetic nanoparticles was an increase in the intensity of specific bands hydroxyl groups as follows: Fe (III) / Ni (II) <Fe (III) / Fe (II) <Fe (III) / Co (II) and the absence thereof in the range of 3100 -3500 cm-1 in the nanoparticles Fe (III) / Ni (II).

Applications of magnetic nanoparticles

In this study we have conducted a series of experiments which tested the performance of magnetic nanoparticles of the type Fe (III) / Fe (II), Fe (III) / Co (II) and Fe (III) / Ni (II) in terms of reducing the content of biomass in surface waters.

Performances of the magnetic nanoparticles were demonstrated in Jar-Test experiments type, followed by the analysis of the chemical parameters (turbidity, pH, conductivity, organic matter) and biological parameters (phytoplankton and zooplankton).

Jar-Test experiments were conducted on surface water and river water, that ha a number of parameters phisio-chemical measures prior to starting the tests, turbidity, pH, temperature, potassium permanganate index and also knowing the load weight of the biological load thereof, (98% Microcystis).

Were used as coagulation solutions aluminum sulfate, mixtures of sulfate and aluminum nanoparticles Fe (III) / Fe (II), aluminum sulfate nanoparticles Fe (III) / Co (II), aluminum sulfate nanoparticles Fe (III) / Ni (II), aluminum polychloride (PAX) and mixtures of PAX nanoparticles Fe (III) / Fe (II), PAX nanoparticles Fe (III) / Co (II), PAX nanoparticles Fe (III) / Ni (II).

In the tables below are the results obtained to determine both the optimal dose of coagulant starting from parameter values of raw water from the river, measured before testing but also the results of Jar-Test type experiments conducted with solutions of coagulants and coagulant with magnetic nanoparticles synthesized in the laboratory.

Physico-chemical and biological raw water (river) were:

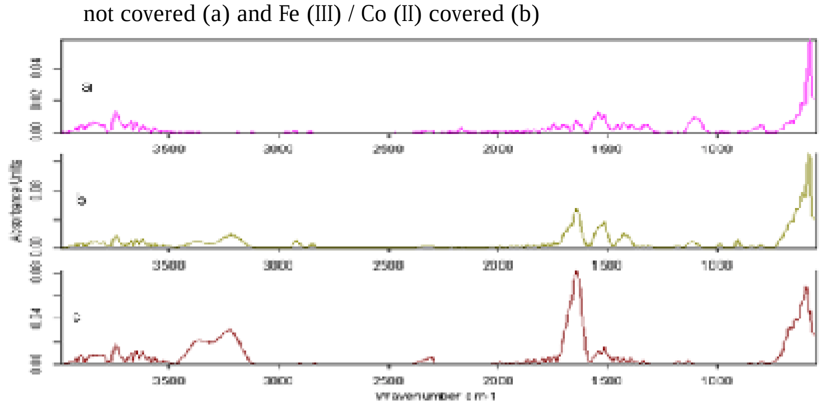

Fig. 3. FTIR spectra of magnetic nanoparticles of Fe (III) / Ni (II) (a), Fe (III) / Fe (II) (b) and Fe (III) / Co (II) (c)

Dose Coagulant (mg/L)	10	20	30	40	50	60	70	80
Potassium permanganate index (mgO_2/l) - SA	8,00	6,08	5,12	4.16	3.20	2.88	3.84	4.86
Phytoplankton (org./l) - SA	48 960	39 760	32 421	30 040	29 160	28 421	31 020	32 400
Zooplankton (org./l) - SA	10 880	11 360	12 200	9 600	8 880	11 200	12 800	14 200
Potassium permanganate index (mgO_2/l) - PAX	3.20	1.76	1.44	1.60	1.92	2.08	3,04	4,00
Phytoplankton (org./l) - PAX	27 320	26 000	14 880	18 620	29 420	32 400	35 520	53 120
Zooplankton (org./l) - PAX	11 200	8 600	4 260	10 200	12 800	14 200	23 680	39 920

Table 2
EXPERIMENTAL DATA OBTAINED FROM TESTED IN WHICH THE JAR TEST USED AS A COAGULATION SOLUTION OF ALUMINUM SULFATE OF 10% CONCENTRATION (SA) AND 10% ALUMINUM POLYCHLORIDE (PAX)

- 110 NTU Turbidity,
- *p*H 8.50, temperature 20ºC,
- Conductivity 275 µS / cm,
- Potassium permanganate index 4 mgO_2 / L,
- Phytoplankton 111 360 org / L
- Zooplankton 20,880 org / l (98% Microcystis).

Optimal doses for use coagulants were established by Jar-Test method and are presented in table 2 and graphs 4, 5 and 6 shown below.

Tests for determining the optimal dose of coagulant, following the parameters and biological oxidability show that, in the case of aluminum sulfate, the best results for a dose is 60 mg/L. For aluminum polychloride, the optimal dose resulting from analysis of the same parameters is 30 mg/L.

Potassium permanganate index (oxidability) values vary downward to 2.88 mgO_2/L for aluminum sulfate, according to the values obtained by biological analysis, phytoplankton and zooplankton, indicating that the value of the optimal dose is 60 mg / L.

The same potassium permanganate index (oxidability) values vary downward to 1.44 mgO_2/L for aluminum polychloride, according to the values obtained by biological analyzes, phytoplankton and zooplankton, indicating that the value of the optimal dose is 30 mg/L.

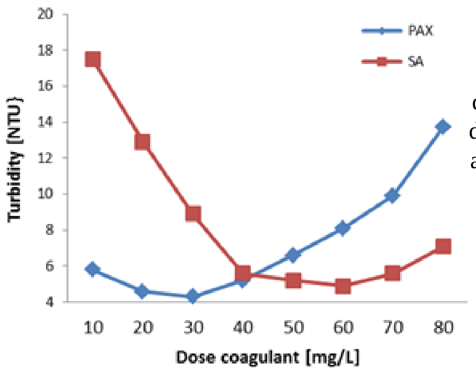

Fig. 4. Turbidity variation depending on the dose of coagulant: aluminium sulfate (SA) and aluminum polychloride (PAX).

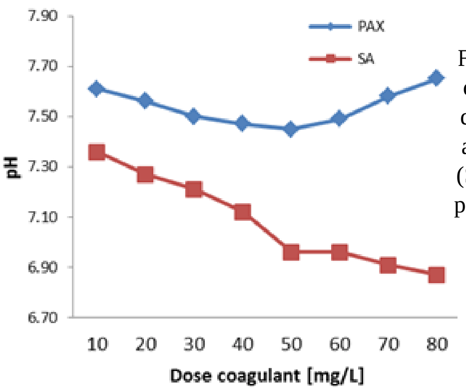

Fig. 5. *p*H variation depending on the dose of coagulant: aluminium sulfate (SA) and aluminum polychloride (PAX).

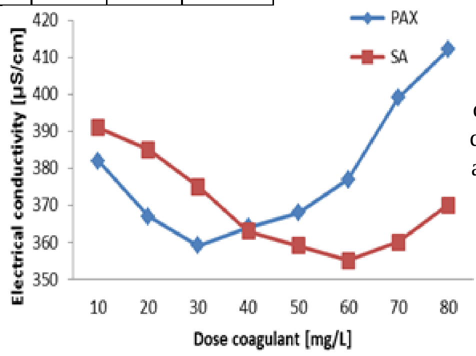

Fig. 6. Conductivity variation depending on the dose of coagulant: aluminium sulfate (SA) and aluminum polychloride (PAX)

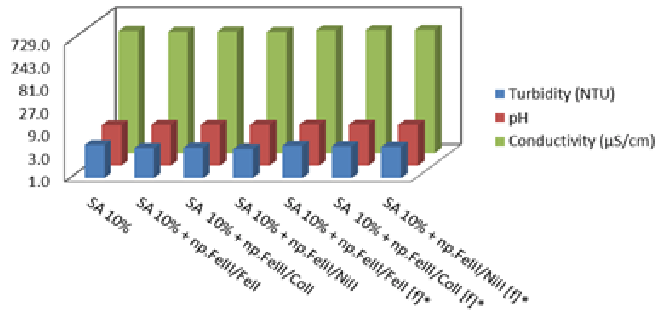

Fig. 7. Turbidity, *p*H and conductivity variation depending on the nature of coagulant: aluminum sulfate (SA) simple and mixtures thereof with magnetic nanoparticles (Fe (III) / Fe (II), Fe (III) / Co (II) and Fe (III) / Ni (II)) unfunctionalized or functionalized *

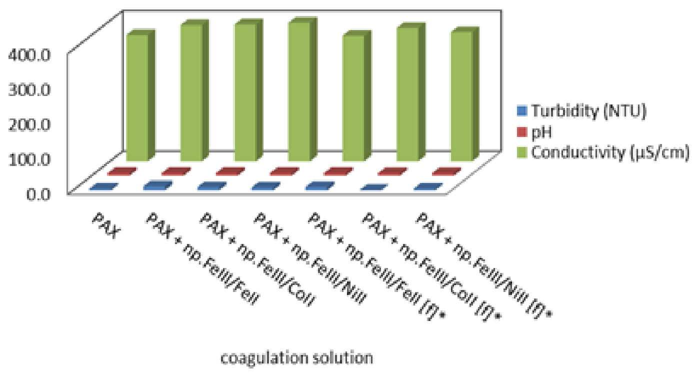

Fig. 8. Turbidity, *p*H and conductivity variation depending on the nature coagulant: aluminum polychloride (PAX) simple and mixtures thereof with magnetic nanoparticles (Fe (III) / Fe (II), Fe (III) / Co (II) and Fe (III) / Ni (II)) unfunctionalized or functionalized

Other physico-chemical parameters were analyzed to establish the optimal dosage of coagulants.

The values obtained by chemical analysis of the parameters turbidity, *p*H and electrical conductivity, made on same samples that went throuth Jar-Tests show for each of the two coagulants, that the optimal dose, is 60 mg/L for sulfate aluminum and 30 mg/L for aluminum polychloride (fig. 7).

It can be seen that mixtures of aluminum sulfate nanoparticles Fe(II)/Ni(II) unfunctionalized has registered the lowest value for the parameters turbidity, pH and conductivity compared with the mixture of the same type of nanoparticles unfunctionalized, but also versus other types of mixtures aluminum sulfate (fig. 8).

In terms of efficiency of the coagulation solution of PAX simple and mixtures with magnetic nanoparticles that are based on Fe, Co and Ni salts on physico-chemical parameters we demonstrated that the coagulation solutions made of PAX mixtures of magnetic nanoparticles functionalized have higher efficiency than simple aluminum polyvinyl magnetic nanoparticles and mixtures thereof with crude. Thus, for the turbidity it is optimal use of the solution for coagulation made of mixtures of PAX with magnetic nanoparticles Fe (III) / Co (II), functionalized compared to the *p*H and conductivity where a high efficiency have mixtures of PAX with magnetic nanoparticles Fe (III) / Ni (II), functionalized, respectively with magnetic nanoparticles PAX Fe (II) / Fe (III) functionalized.

Conclusions

In this paper we have synthesized and characterized structurally and compositionally magnetic nanoparticles based on iron, cobalt and nickel salts and we studied their effectiveness in reducing biomass in surface water.

Based on the experiments carried out it was proved that the use of magnetic nanoparticles in aluminiu sulfate coagulant solutions types or aluminum polychloride considerably reduces, till up to 95%, the biological mass of a surface waters.

Functionalized magnetic nanoparticles efficiency is greater if their inclusion in aluminum polychloride coagulant type than if in aluminum sulfate.

To obtain coagulant solutions, the percentage of the nanoparticles mass is much lower for aluminum nanoparticles used in aluminium polychloride (0.01%) than in aluminum sulfate (0.1%).

Effectiveness of the nanoparticles embedded in aluminium sulfate and aluminum polychloride used in water treatment for removal of biomass with high content of blue algae (namely Microcystis) can be classified as follows: as the most homogeneous and with good results were solutions with nanoparticles functionalized on the basis of nickel, followed by the cobalt, and only after the iron and the physico-chemical parameters.

In terms of physico-chemical parameters there was an improvement in their values when we used magnetic nanoparticles solutions coagulants compared to simple solutions.

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