Removal of metallic ions from water by use of PS-PEO diblock copolymer stabilized magnetite particles

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Abstract

Due to non degradable, cumulative and toxic effects in living organisms, metals such as copper, zinc, magnesium, calcium and barium, bring the permanent contamination to the ecosystem, environment, and human health.

In this work, magnetite particles (Fe_3O_4) were stabilized with diblock copolymer polystyrene (PS)–poly (ethylene oxide) (PEO), to yield (Fe_3O_4-PS-PEO), and then they were used as adsorbent for the remediation of metal ions such as Cu(II), Zn(II), Mg(II), Ca(II) and Ba(II), present in contaminated water.

The magnetite stabilisation by the copolymer is expected to produce adsorbent having large specific surface areas, high adsorption rate and high capacity of metal removal from wastewater.

Thus, aqueous dispersions of magnetite particles, Fe_3O_4, were first stabilized in the presence of PS-PEO diblock copolymer. Further, the presence of non-ionic copolymer did not alter the sign of the Fe_3O_4 particles surface charge, and leads to electro steric stabilization of the iron oxide dispersions in water. Thereafter, the modified magnetite particles (Fe_3O_4-PS-PEO) were used as adsorbent for the removal of divalent cations such as Cu(II), Zn(II), Ba(II), Ca(II) and Mg(II), from contaminated water.

The adsorption of various metals on Fe_3O_4-PS-PEO adsorbent was assessed by titrating the magnetite particle aqueous dispersions with standardized metal aqueous solutions, and monitoring the Streaming Induced Potential (SIP), using a potential measuring device (Particle Charge Detection, PCD, Müteck instrument). The data indicate that, in all instances, upon adsorption of the divalent cation to the solid adsorbent Fe_3O_4-PS-PEO, the magnitude of the SIP value decreased with increasing metal concentration, and reached plateau value. However, the variation of the SIP was found to depend on various parameters such as the nature of the divalent cation, and the amount of iron oxide. The results of the adsorption experiments indicate that about 70 to 85 wt% of cupric ions, (Cu(II)), could be removed from the polluted water thanks to the use of the Fe_3O_4-PS-PEO stable aqueous dispersion.

Keywords: Iron oxide, textile effluent, particle size, surface coating, copolymer, streaming induced potential.

1. Introduction

Pollution of water by organic and inorganic substances has become very worrying today. Heavy metals such as chrome, copper, lead and zinc, contribute to this pollution since they are non-biodegradable and toxic species. In fact, these metals are continually discharged into the aquatic ecosystems, as resulting from various human activities, and their accumulation in the environment has negative effects on the human health. It is therefore essential to develop efficient adsorbents allowing the removal of these heavy metals from polluted water.

Various methods such as chemical oxidation, reverse osmosis, coagulation–flocculation, filtration, adsorption, and photo degradation have all been applied to effluent treatment, yet vary in their effectiveness, cost, and environmental impact [1]. Overall, adsorption has been the most competitive of these methods because of its simplicity, high efficiency, and availability [2]. Many materials have been made available for this process [3], with absorbents containing natural biopolymers such as chitosan drawing particular interest recently [4]. However, these adsorbent materials can accumulate in the discharge, resulting in secondary pollutants [4]. Therefore, developing magnetic adsorbents which will be more easily separable would significantly improve the process [5].

During last decades, the application of iron oxides nanoparticles has grown radically, in several relevant fields such as medicine, electronics, and mainly in environmental remediation [6-8]. However, in the environmental field, the main problem occurring with the use of pure iron oxide nanoparticles, as an adsorbent of pollutants in water remediation, is their low stability and/or their flocculation and sedimentation in the aqueous media. To overcome these limitations, the surface of the nanosized magnetite particles should be modified with organic or inorganic moieties in order to stabilize them in aqueous suspensions.

The aim of the present work is to investigate the effect of non-ionic copolymer such as polystyrene–poly (ethylene oxide) diblock copolymer (PS-PEO), on the particle size and the surface charge of iron oxide nanoparticles. Subsequently, the modified magnetite particles (Fe_3O_4-PS-PEO), are expected to have controlled sizes and surface charges, and will suitable as adsorbent for the remediation of metal ions such as Cu(II), Zn(II), Mg(II), Ca(II) and Ba(II), present in contaminated water.

2. Experimental

2.1. Materials

The reagents used in the present work were purchased from various commercial sources. The iron oxide used (Fe_3O_4) having elemental particle size of 50 nm in diameter was purchased from Aldrich. The diblock copolymer used polystyrene-polyethylene oxide (1000-3000) was the same as used elsewhere [9]. The various divalent salts, $CuCl_2$ (Aldrich), $MgCl_2$ (Aldrich), $ZnCl_2$ (Aldrich), $BaCl_2$ (Prolabo), and $CaCl_2$ (Prolabo), were used as received without further purification.

2.2. Methods

2.2.1. Zeta potential measurements

The measurements of the electrophoretic mobility (Ue) of the Fe_3O_4 and Fe_3O_4-PS-PEO particles were performed in a clean electrophoresis chamber, filled with the colloidal aqueous dispersion and submitted to an electrical field for a few seconds. The tension applied in the electrophoretic cell was 100 V, [10].

2.2.2. Streaming Induced Potential, SIP, measurements

The removal efficiency of various divalent cations, Cu(II), Zn(II), Mg(II), Ca(II) and Ba(II) from the salted aqueous solutions onto the Fe_3O_4-PS-PEO particles, was evaluated by titration of the Fe_3O_4-PS-PEO aqueous dispersion with the respective salt, $CuCl_2$, $ZnCl_2$, $MgCl_2$, $CaCl_2$ and $BaCl_2$, and by using a potential measuring device (particle charge detection, PCD, Müteck instrument) as described elsewhere [10]. It should be mentioned that the PCD Müteck instrument allows the measurement of only relative potential values, [11].

2.2.3. Particle size measurements

The particle size of Fe_3O_4 aqueous dispersions in the presence of the PS-PEO copolymer, and in the absence or the presence of various divalent cations, Cu(II), Zn(II), Mg(II), Ca(II) and Ba(II), were measured by dynamic light scattering (DLS), using Coulter Model N4S (Coultronics) apparatus [12, 13].

2.3. Preparation of Fe_3O_4 and Fe_3O_4-PS-PEO particles aqueous dispersions

A known amount of PS-PEO copolymer was dissolved in deionized water, the resulting mixture was heated at 80 °C and then cooled to ambient temperature to yield a final copolymer concentration of 10.023 g/L. The aqueous dispersion of iron oxide, Fe_3O_4, was prepared by dissolving 50 mL of Fe_3O_4 in 50 mL of deionized water and then stirred for 24 h to yield homogenous aqueous dispersion of 1 g/L of Fe_3O_4. Subsequently, two Fe_3O_4-PS-PEO particles aqueous dispersions were prepared by mixing, respectively, 1 ml (dispersion A) and 2 ml (dispersion B) of the Fe_3O_4 aqueous dispersion, with 80 ml of PS-POE aqueous solution.

2.4. Batch adsorption experiments

Perkin Elmer Lambda 750 UV-Vis spectrometer was used to study the effect of $CuCl_2$ concentration on the adsorption of cupric ions, Cu(II), and/or their removal from water by using Fe_3O_4-PS-PEO solid as adsorbent. The adsorption isotherm was assessed by analysing the remaining Cu(II) amount in the supernatant, as obtained by centrifuging the Fe_3O_4-PS-PEO-$CuCl_2$ aqueous dispersions at 20000 rpm. The equilibrium $CuCl_2$ concentrations were determined by the use of a calibration curve based on Beer's law and the measured absorbance of various $CuCl_2$ aqueous concentrations at wavelength λ=810 nm

3. Results and discussions

3. 1. Zeta potential

Zeta potential values, as function of the aqueous phase pH, are shown in Fig. 1 for the magnetite particle in the absence of the copolymer. The data indicate that the iron oxide particle has both positively and negatively charged groups, as resulting from the amphoteric character of the Fe_3O_4 surface. In addition Fig. 1 indicates at the pH value around 3.8, the particle zeta potential is zero and this pH value corresponds to the isoelectric point (PIE) of the magnetite particles studied in the present work. Fig. 2 shows the zeta potential values of the magnetite particles in the presence of the PS-PEO copolymer. Accordingly, the Fe_3O_4-PS-PEO particles bear negative zeta potential values even in the presence of the PS-PEO copolymer, this means that the copolymer does not reverse the sign of surface charge density of the magnetite particles for the entire polymer concentration range investigated. However, at high copolymer concentration, the zeta potential reaches a plateau (about -3 mV) as can be seen in Fig.2. The decrease in the zeta potential magnitude as shown in Fig. 2 is due to the displacement of the shear plane towards the bulk solution.

Fig. 1

Fig. 2

Fig. 3 shows an illustration of the copolymer adsorption from water onto the Fe_3O_4 surface to yield Fe_3O_4-PS-PEO electro sterically stabilized magnetite particles.

Fig. 3

3.2. Size and morphology of Fe_3O_4 aggregates in the absence and presence of the PS-PEO copolymer

Figs 4 and 5, show, Transmission Electronic Microscopy (TEM) images of Fe_3O_4 aggregates as prepared, respectively, in the absence and in the presence of PS-PEO copolymer.

Fig. 4

Fig. 5

As can be seen in Fig 4, in the absence of PS-PEO copolymer, the Fe_3O_4 elemental nanoparticles form aggregates having compact structure, whereas Fig. 5 shows that in the presence of the non-ionic copolymer, Fe_3O_4 nanoparticles form aggregates having less compact and porous structure. It should be noted that the pore size in Fig. 5 is are larger than the one of Fe_3O_4 aggregates, prepared in the absence the copolymer, as depicted in Fig. 4. Such Fe_3O_4 aggregates, as prepared in the presence of copolymer, lead to small particle size in water.

3.3. Streaming Induced Potential, SIP

Fig. 6 presents the variation of Streaming Induced Potential (SIP) of Fe_3O_4-PS-PEO particles versus the amount of added divalent salt ($CaCl_2$, $BaCl_2$, $MgCl_2$, $ZnCl_2$, $CuCl_2$) at constant initial salt concentration=0.1 M.

Fig. 6

The curves in Fig. 6, show in all instances, decrease in the magnitude of the initial Fe_3O_4-PS-PEO particle SIP value, and various initial slope values depending on the nature of the divalent cation. As can be observed in the figure, divalent cations such as Mg^{2+} exhibit greater decrease of Fe_3O_4-PS-PEO particle surface charge as compared to Ca(II), Ba(II), Zn(II) and Cu(II), without the solid surface charge sign reversal. It should be noted that prior the addition of the salt solution, the pH of the Fe_3O_4-PS-PEO aqueous dispersion was adjusted to pH around 12, by adding small amounts of sodium hydroxide (NaOH) aqueous solutions. Therefore, it is likely that under this pH condition, the metal ions (Mg(II), Ca(II), Ba(II), Zn(II) and Cu(II)), undergo hydrolysis, leading to the formation of metal–hydroxide complexes in the suspension. Each hydrolysable metal ion has a distinct pH and concentration where it first hydrolyses. The first hydrolysis constants (pK_1) of Mg, Cu Zn, Ba, and Ca, are, respectively, 11.02, 7.90, 8.99, 9.85, and 10.96. Thus, at the pH value of the Fe_3O_4-PS-PEO aqueous dispersion which is about 12, i.e. above the pK1 values of Cu and Zn, the extent of Cu and Zn, hydrolysis should be important. It is noteworthy to note that in highly alkaline Fe_3O_4-PS-PEO suspension, a net negative charge on the solid surface occurs, leading to accumulation of the added heavy metals within the diffuse part of the electrical double layer. Thus, although the concentration of the metal ion in solution may be much less than the solubility limit with respect to metal hydroxide and oxide solids, the solubility limit near the solid surfaces is exceeded and precipitation onto the solid surface takes place. In addition, at high pHs, the measured zeta potential and found IEP do not belong to the Fe_3O_4-PS-PEO, but they are the IEP of the precipitate, which are 12-13 for $Mg(OH)_2$, and for the difference in behaviour shown in Fig 6, of Fe_3O_4-PS-PEO particles in the presence of various cations is related to the different IEP values of various metal hydroxide formed.

3.4. Particle size

Figs. 7 and 8 show, respectively, the effects of Fe_3O_4 amount and $MgCl_2$ concentration, on the Fe_3O_4-PS-PEO particle size in aqueous medium.

Fig. 7

Fig. 8

Hence, in the absence of copolymer and salt, the Fe_3O_4 aqueous dispersion at pH=12, was unstable giving aggregates sizes around 700 nm. However, stable aggregates having smaller sizes, in the range: 61-612 nm were obtained in the presence of PS-PEO copolymer as shown in Fig. 7. The aqueous dispersions A and B (see paragraph 2.4) give Fe_3O_4-PS-PEO particle sizes of, respectively, 61 nm and 204 nm. Further, as can ne observed in Figs. 7 and 8, in the absence of Fe_3O_4, the micelle size of the PS-PEO aqueous solution (10.023 g/L), at ambient temperature, was about 50 nm. Upon addition of increased amount of Fe_3O_4 to the PS-PEO aqueous solution, adsorption of the diblock copolymer from water onto Fe_3O_4 occurred, leading to formation of stabilized Fe_3O_4-PS-PEO particles, as depicted in Fig. 3.

Fig. 7 shows that for the aqueous dispersions A and B, in the presence of increased amount of the $MgCl_2$ divalent salt, the Fe_3O_4-PS-PEO particle size was found to increase, reaches a maximum value, and then decreases at high salt concentration. Similar behaviours were observed in the presence of $CuCl_2$, $ZnCl_2$, $CaCl_2$ and $BaCl_2$ salts. The increase of the particle size at low salt salt concentration results from the reduction in the electrical double layer thickness (ionic strength effect), and the screening of the solid particle surface charges, by the divalent cations, leading hence to less electrical repulsion between the Fe_3O_4-PS-PEO solid particles, as depicted in Fig. 9. However, the Fe_3O_4-PS-PEO particle size decreases at high salt concentration. Such decrease at high salt concentration, is likely due to the metal hydrolysis and/or the formation of negatively charged metallic precipitates ($Mg(OH)_2$, $Cu(OH)_2$ $Zn(OH)_2$ $Ca(OH)_2$ $Ba(OH)_2$) which will be then repelled from the negatively charged Fe_3O_4-PS-PEO solid surface, as schematically presented in Fig. 9. The formation of these metallic precipitates will consume the divalent cation accumulated and/or adsorbed at the Fe_3O_4-PS-PEO solid-water interface, reducing hence the ionic strength of the medium and decreasing finally the Fe_3O_4-PS-PEO particle size (Fig. 9).

3.5. Adsorption and removal from water of cupric ions Cu(II) Fe_3O_4-PS-PEO particles as solid adsorbent

The adsorption and removal from water, of cupric ions, Cu(II), onto Fe_3O_4-PS-PEO particles were studied at seven increasing initial Cu(II) concentrations, as shown in Fig 10 and Fig. 11.

Fig. 10

Fig. 11

As can seen in Fig. 10, copper adsorption increased with the enhancement of copper concentration up to 86 mg of cupric ions per g of Fe_3O_4-PS-PEO and the maximum wt% of the removed cupric ions is about 85% (Fig. 11). The higher adsorbed amount of cupric ions from water onto the Fe_3O_4-PS-PEO solid surface, is due to the stabilization of Fe_3O_4 particles by the PS-PEO copolymer. A comparison with the literature indicates that the present stabilized magnetite particles perform better in terms of copper adsorption than many other adsorbents such as Chestnut shell (5.5 mg/g) [14], Grape stalk wastes (10.1 mg/g) [15], and Kaolinite (10.8 mg/g) [16].

Conclusion

The present study demonstrates the capability and effectiveness of the Fe_3O_4-PS-PEO particles, used as adsorbent for removal of heavy metals, such as Cu(II), Zn(II), Ba(II), Ca(II) and Mg (II), from water. Based on the obtained results, a probable mechanism for uptake of the metal ions can be electrostatic attraction. Due to the enhanced stability of the magnetite particles by the copolymer adsorption, a higher adsorbed amount (86 mg/g) of cupric ions from water onto the Fe_3O_4-PS-PEO solid surface was obtained. A comparison in the literature, indicates that the stabilization of the magnetite particles by the PS-PEO copolymer, improves the copper removal from contaminated water.

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Figures and Tables captions

Fig. 1 Zeta potential of Fe_3O_4 nanoparticles versus the aqueous phase pH in the absence of the PS-PEO

Fig. 2 Zeta potential of Fe_3O_4 nanoparticles versus increasing amounts of PS-PEO.

Fig. 3 Schematic illustration of the mechanism of the electro steric stabilization and particle size reduction of Fe_3O_4 particles by PS-PEO copolymer in aqueous medium.

Fig. 4: Transmission Electronic Microscopy image of Fe_3O_4 aggregates, as prepared in the absence of the PS-PEO copolymer

Fig. 5: Transmission Electronic Microscopy image of Fe_3O_4 aggregates, as prepared in the presence of the PS-PEO copolymer

Fig. 6 Titrating of Fe_3O_4-PS-PEO sample with various divalent cations. SIP versus the amount of added salt expressed in microliters (initial salt concentration= 0.1 M).

Fig. 7 Effect of Fe_3O_4 amount on the Fe_3O_4-PS-PEO particle size

Fig. 8 Effect of $MgCl_2$ concentration, on the Fe_3O_4-PS-PEO particle size

Fig. 9 Schematic representation explaining the evolution of the Fe_3O_4-PS-PEO particle size as function of the salt concentration

Fig. 10 Adsorption isotherm of Cu(II) ions from water onto Fe_3O_4-PS-PEO particles

Fig. 11 Removal percentage of Cu(II) ions from water onto Fe_3O_4-PS-PEO particles

Fig. 1

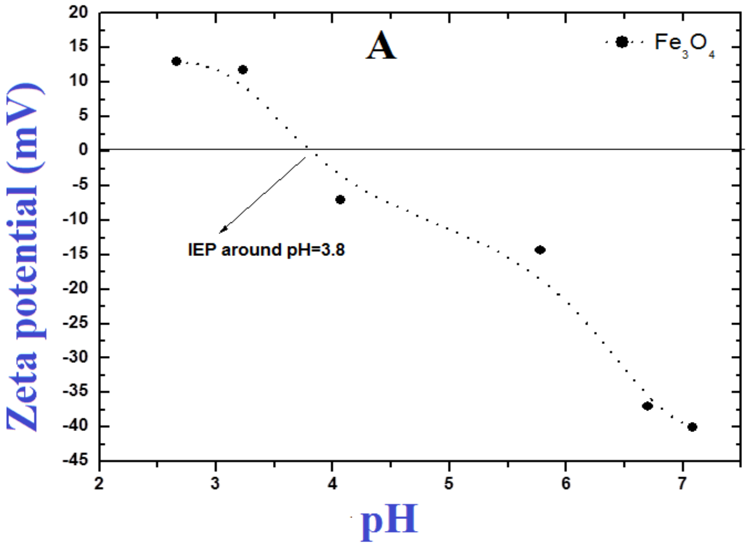
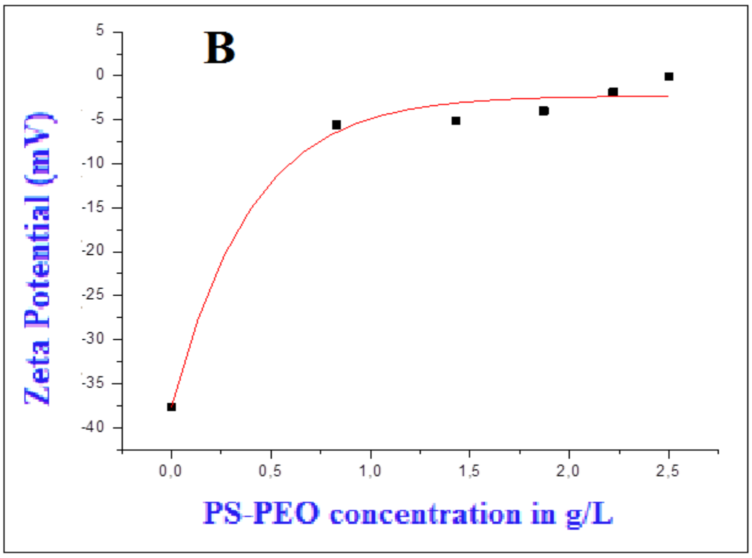

A
Fe$_3$O$_4$
IEP around pH=3.8
Zeta potential (mV)
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
2
3
4
5
6
7
pH

Fig. 2


B
Zeta Potential (mV)
5
0
-5
-10
-15
-20
-25
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0,0
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2,0
2,5
PS-PEO concentration in g/L

Fig. 3

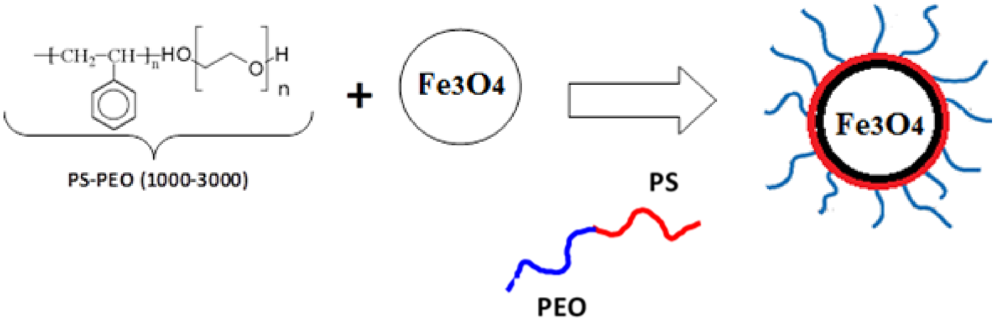

Fig.4

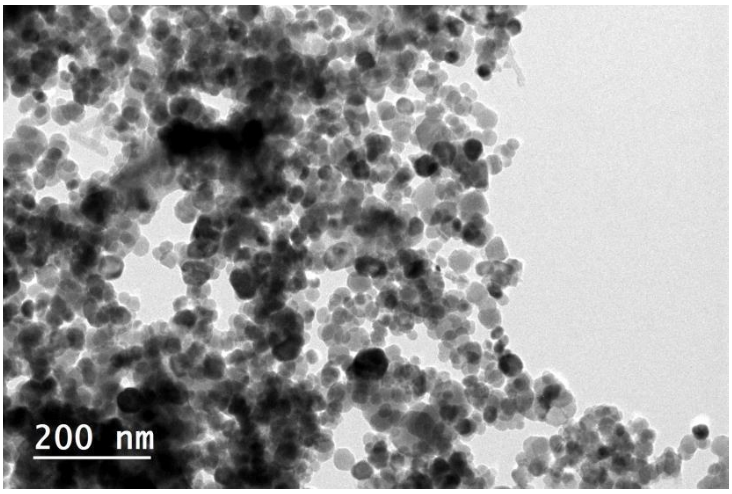

Fig. 5

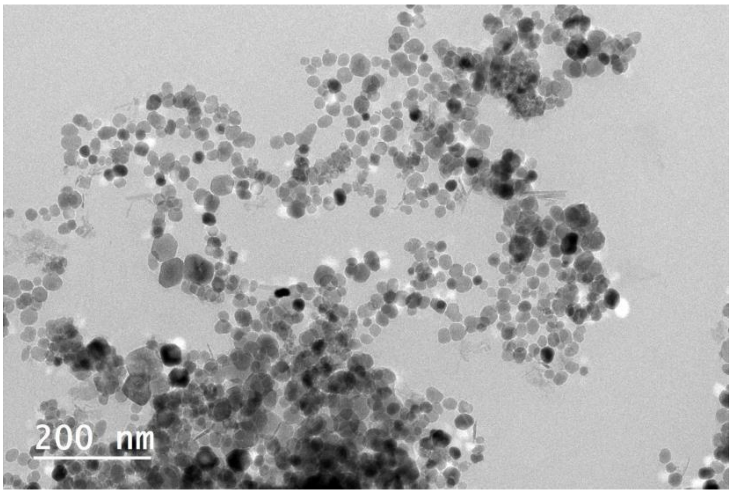

Fig. 6

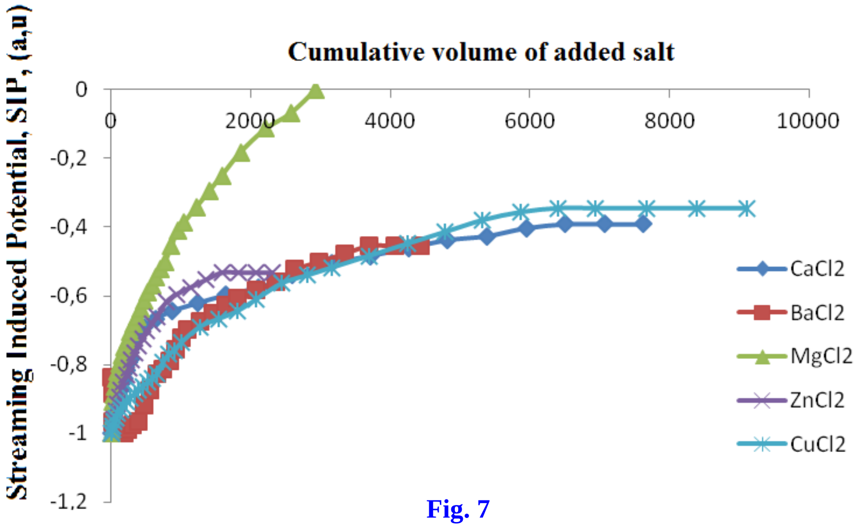

Fig. 7

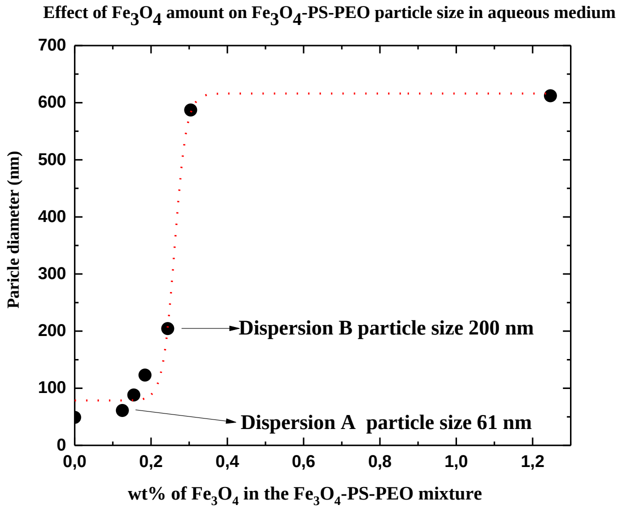

Fig. 8

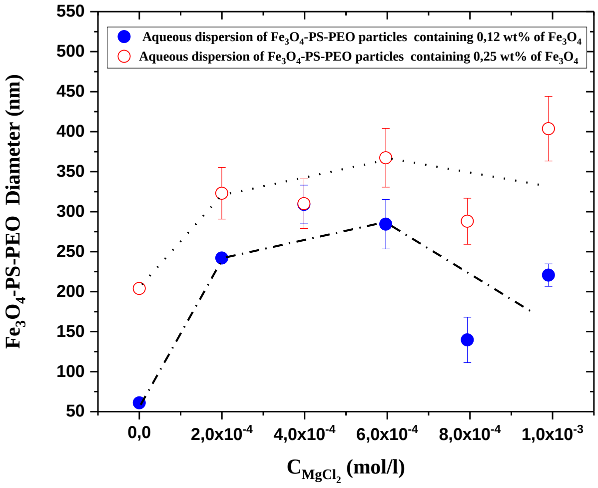

Fig. 9

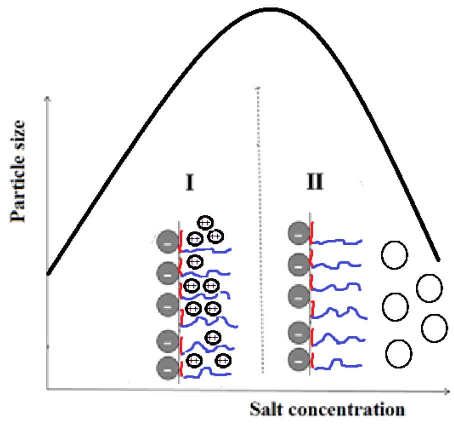

Fig. 10

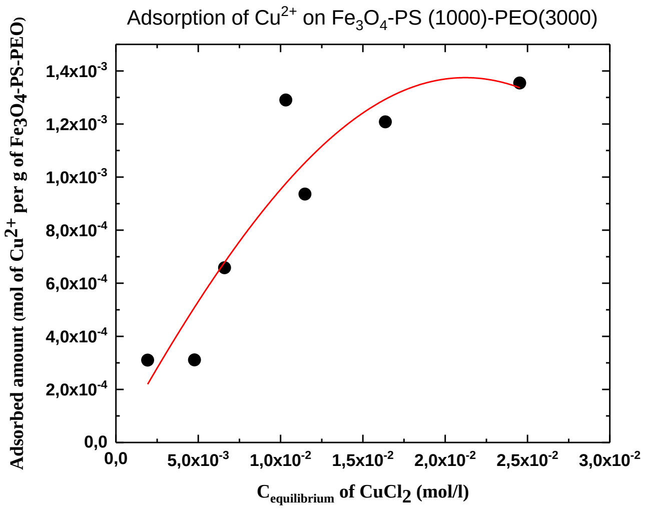

Fig. 11