

# Preparation and characterization of PEG bis(amine) grafted PMMA/SPION composite nanoparticles

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## ABSTRACT

We report novel magnetic composite nanoparticles for heavy metal ion separation. Superparamagnetic iron oxide nanoparticles (SPIONs) and were coated with poly(methylmethacrylate) (PMMA) by emulsion polymerization process in the aqueous suspension of SPIONs. In addition, the hydrolysis of carboxylic functional groups onto the PMMA-coated SPIONs was grafted with Polyethylene glycol *bis(amine)*. Then, the functional group structures were investigated by Fourier transforms infrared spectroscopy (FTIR). The morphology of PMMA/SPIONs was determined by transmission electron microscopy (TEM) and atomic force microscope (AFM). The magnetic property was investigated by the vibrating sample magnetometer (VSM). The metal concentration in the solution after separation using the nanoparticles was determined by inductivity coupled plasma optical emission spectrometer (ICP-OES). Furthermore, we demonstrate that the efficiencies of the heavy metal ion removal for Cu(II), Mn(II), Zn(II), Cd(II), Pb(II), Co(II) and Ni(II) are 80.0 %, 57.7 %, 54.3 %, 40.0 %, 34.8 %, 32.5 % and 30.2 % by weight, respectively. The nanoparticles also exhibit some selectivity for copper, manganese and zinc. The results show that the composite nanoparticles are extremely promising for heavy metal ion separation. Copyright © 2016 VBRI Press.

**Keywords:** SPIONs; PMMA; composite nanoparticles; heavy metal removal; surface modification.

## Introduction

Recently, heavy metal ion separation from aqueous solutions based on the coordinating interaction with surface modified magnetic nanoparticles has been studied by several groups [1 - 4]. The advantage of SPIONs for heavy metal separation is based on their high surface area, fast separation rate, and easy separation simply by applying external magnetic fields [5-8].

Various methods have been applied to coat coated nanoparticles with polymers. Many studies attempted direct coating of polymer chains onto nanoparticle surface; however, this lead to high agglomeration, rendering unsuitable for waste water treatment application [9, 10]. In this research poly(methylmethacrylate) (PMMA) was selected as the based coating materials. The physical durability of PMMA is far superior to that of other thermoplastic. PMMA can be coated onto the SPIONs surface and grafted with organic matter. The aim of this study is to prepare PMMA/SPIONs nanoparticles and graft PEG *bis(amine)* as potential and beneficial adsorbents to remove heavy metal pollutants from waste water. Emphasis

is laid on the use of PMMA shells as the supporting layer and PEG bis(amine) as graft, with the functional amine groups, easily coated onto the surface of particles and accessed by heavy metal ions.

The surface morphology of PEG-bis(amine) grafted PMMA/SPIONs nanoparticles was characterized by using transmission electron microscope (TEM) and atomic force microscope (AFM). We also examine the efficiency function of the composite nanoparticles for removal of Cu(II), Mn(II), Zn(II), Cd(II), Pb(II), Co(II) and Ni(II) ions from aqueous solutions.

## Experimental

### Materials

The chemicals used for preparing PMMA/SPIONs composite nanoparticles and surface modification were methyl methacrylate (MMA, 99 %) monomer supplied by Italmar (Thailand) Co. Ltd., sodium dodecyl sulfate, (SDS, BDH) used as surfactant, potassium persulfate of chemical grade from Aldrich used as the initiator, 1-ethyl-

3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC, MW191.7) and N-Hydroxylsuccinimide ester (NHS, MW 115.1, Aldrich) used as the coupling reagent. The chemicals used for grafting on PMMA/SPIONs were polyethylene glycol *bis(amine)* (EGDMA, Sigma Aldrich), (MW2,000). Tetrahydrofuran (THF, HPLC grade, Fisher Scientific, lithium hydroxide (LiOH, Sigma Aldrich), hydrochloric acid (HCl, Sigma Aldrich), Fisher Scientific) and 2-morpholinoethane sulfonic acid (MES, Fluka).

Superparamagnetic iron oxide nanoparticles (SPIONs), provided by LTP, EPFL Switzerland, were prepared by the alkaline co-precipitation of ferric and ferrous chlorides in aqueous solution, as described elsewhere in detail [9]. All the reagents were used without any treatment except the MMA monomer, in which the removal of the hydroquinone inhibitor was required.

The inorganic chemicals, including copper(II) acetate monohydrate  $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$  (ACROS (6046-93-1), lead(II)acetatetrihydrate  $\text{Pb}(\text{C}_4\text{H}_6\text{O}_4) \cdot 3\text{H}_2\text{O}$  (Sigma-Aldrich(215902), cadmium(II)acetate dehydrate  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (Sigma-Aldrich(289159)), manganese(II) acetate tetrahydrate  $(\text{CH}_3\text{COO})_2\text{Mn} \cdot 4\text{H}_2\text{O}$  (Aldrich(22100-7)), cobalt(II) acetate tetrahydrate  $\text{Co}(\text{C}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O})$  (Fluka (60790) and zinc(II) acetate dihydrate  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  Sigma-Aldrich (96459), were of analytical grade and purchased from Italmar (Thailand) Co. Ltd.

#### Preparation of PMMA/SPION composite nanoparticles

The PMMA/SPIONs was prepared in an aqueous suspension of SPIONs and 200 mg SDS. It was diluted in 10 ml DI water and fed into a three-necked flask and then stirred at 450 rpm under  $\text{N}_2$  gas. When the temperature of the aqueous suspension reached 80 °C and maintained by cycling paraffin oil from aqueous thermostat bath, the monomer was slowly added to the three-necked flask 0.12 mg (diluted in 10 ml DI water) of the initiating agent aqueous solution was added to the system and then stir for 6 h. The part suspension was freeze dried at -80 °C in a vacuum freeze drier for the characterizations and future surface modification.

#### Preparation of PEG *bis(amine)* grafted nanocomposites

For the synthetic pathway of PMMA/SPIONs modification, a hydrolysis of carboxylic functional group on the PMMA coated SPIONs was carried out by dispersing 2.5 g LiOH with 420 mL THF under sonication [10-12]. The mixed solution was agitated for 5 h in an inert  $\text{N}_2$  condition. The precipitate was washed with de-ionized water and ethanol [13-15]. The colloids were then freeze-dried. 5mg of the prepared PMMA/SPIONs were dispersed in a vial with 100  $\mu\text{L}$  2-morpholinoethane sulfonic acid (MES, pH6). EDC and NHS were dissolved in 200  $\mu\text{L}$  of a 25 mM 2-morpholinoethane sulfonic acid (MES, pH6) to reach the concentration of 3.2 M and 1.6 M, respectively. Both of solutions were then mixed with prepared magnetic composite nanoparticles and sonicated for 30 min at room temperature. Then 6.4 mg of PEG *bis(amine)* was dissolved in 500  $\mu\text{L}$  of 25 mM 2-2-morpholinoethane sulfonic acid (MES, pH6) [16-18]. This solution was added to the mixture and sonicated for another 30 min. After the

reaction, the grafted PMMA/SPIONs were precipitated by centrifugation at 10,000 rpm and then washed with water and stored in water.

#### Characterizations

The morphology of PMMA/SPIONs composite nanoparticles and their modified surface were characterized by a transmission electron microscope (TEM, Jem-2020 200 keV, JEOL) The high magnification mode was performed for evaluation of uncoated SPIONs, the PMMA coated SPIONs and PEG *bis(amine)* grafting in composite nanoparticles. The samples for TEM observation were sonicated in DI water for 20 min and deposited onto carbon-coated copper grids and air-dried before examination.

AFM investigation started from diluting magnetic nanoparticles in the water and then dropping onto a freshly cleaved mica substrate. The morphology of the magnetic nanoparticle was investigated after drying. This investigation had performed with a tapping mode using NSG 10 cantilever at 190-325 KHz resonance frequency. All images were recorded at room temperature with a scanning rate of 1 Hz and a number of analyzed areas at 256 Pixels.

In addition, to confirm magnetic properties, the particles were analyzed by using Magnetic Force Microscope (MFM, Seiko, Japan) with NSG01-Co cantilever at 115-190 KHz resonance frequency and the force constant in the range of 2.5- 10 N/m.

The chemical structure of magnetic nanoparticles was investigated by using FTIR (Perkin-Elmer). The magnetic properties of materials were measured with a vibrating sample magnetometer (VSM, Lakeshore 7303). The concentration of heavy metal ions in the solution before and after removing the ions was determined by the inductively coupled plasma optical emission spectrometer (ICP-OES Perkin Elmer, Optima 4300DV).

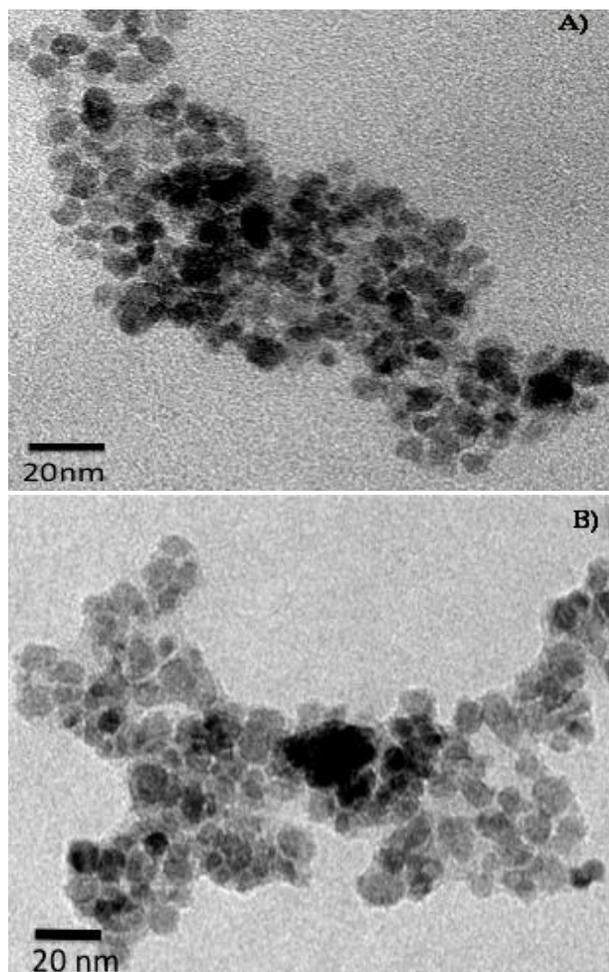
#### Metal solution preparation and removal testing

Metal Cu(II), Mn(II), Zn(II), Cd(II), Pb(II), Co(II) and Ni(II) solutions were prepared by dissolving each metal compound in distilled water at almost 1 mM concentration. The pH of these solutions was not adjusted in the analysis. For removal of heavy metal ions by using PEG *bis(amine)*-grafted SPIONs/PMMA, 200  $\mu\text{L}$  of the composite nanoparticles were dropped into 5 mL of metal solutions with concentration as mentioned above and then sonicated for 1 min. After sonication, a 160 mT external magnetic bar was applied for 5 min to capture heavy metal ions that were adsorbed onto the magnetic composite nanoparticles.

The metal concentration in the solution after removal was determined by inductivity coupled plasma optical emission spectrometer ICP-OES. The morphology of composite nanoparticles with adsorbed heavy metal ions was characterized by AFM (Fig. 2). The removal efficiency rate (%) of metal ions was calculated as follows:

$$\text{Removal efficiency rate (\%)} = (\text{Co}-\text{Ct})/\text{Co} \times 100 \quad (1)$$

where, Co and Ct are the initial and residual concentration of heavy metal ions (mg/L) in aqueous solution, respectively.



**Fig. 1.** TEM image of super paramagnetic iron oxide nanoparticles (SPIONs) (A). TEM image of PEG *bis(amine)* grafted onto PMMA/SPION composite nanoparticles (B).

## Results and discussion

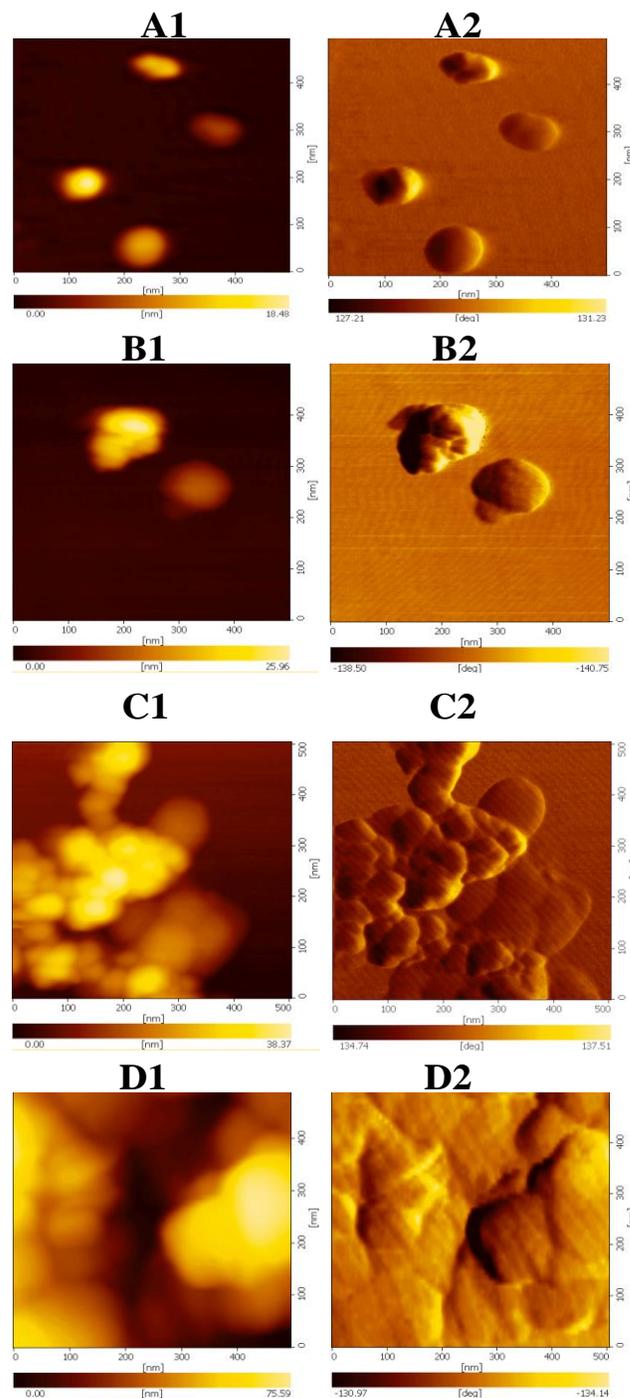
### *The morphology of PEG bis(amine) grafted PMMA/SPIONs*

The TEM image of the bare SPIONs shown in **Fig. 1A** composes of spherical grains with sizes range from 5-9 nm. The polymer matrix with effectively PMMA/SPION composite nanoparticles coating is shown in **Fig. 1B**.

In **Fig. 1B**, the SPIONs cores are surrounded by a layer of materials with a lower contrast, which should be the PMMA grafted with PEG *bis(amine)*. This result is confirmed by the FTIR technique (later discussed). In order to obtain complimentary information, the AFM analysis has been carried out for the magnetic composite nanoparticles at different coating steps. The SPIONs as shown in **Fig. 2 (A1, A2)** have a few agglomeration on the glass support PMMA-coated SPIONs of the particles with size ranging result are similarly observed in **Fig. 1B** be nanoparticle and also between the neighboring nanoparticles.

AFM images in **Fig. 2(B1, B2)** exhibits some aggregation of the particles with size ranging from 20-40 nm. These results are similarly observed in **Fig. 1B**. The aggregation may be a result of the electrostatic forces

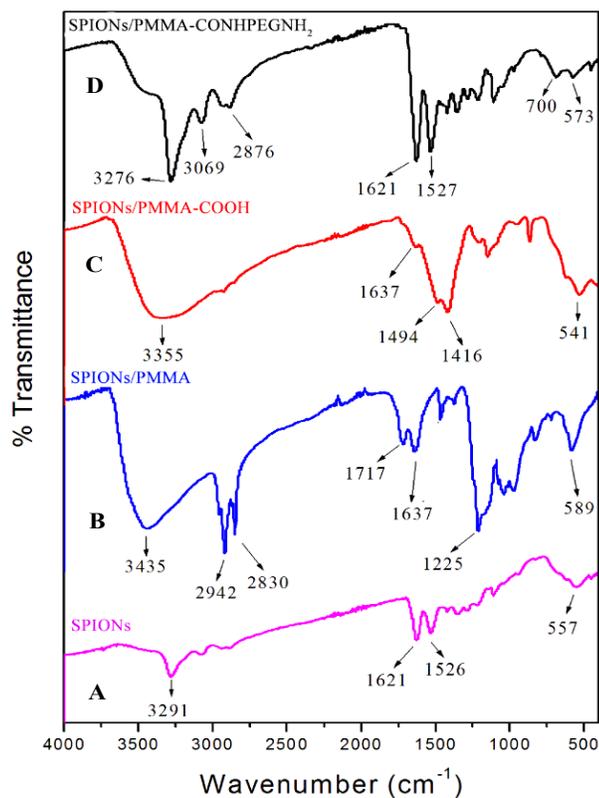
between the substrate and nanoparticles, and also between the neighboring nanoparticles. For the PEG *bis(amine)*-grafted nanoparticle, the PMMA surface, with the carboxylic group, is expected to be readily grafted with PEG *bis(amine)* to form brush-like hydrogel surface. **Fig. 2 (C1, C2)** indicates that the nanoparticles are coated with layers of materials, which should also be responsible to the greater extent of aggregation, as observed. Note the different size distribution and appearance observed by the TEM and the AFM technique.



**Fig. 2.** AFM images ( $0.5 \times 0.5 \mu\text{m}^2$ ) of the composite nanoparticles at different stages: SPIONs (A), SPION coated PMMA nanoparticles (B), PEG *bis(amine)* grafted onto PMMA/SPION composite nanoparticles (C) and the composite nanoparticles with adsorbed Co(II) ions (D).

This probably arise from the agglomeration of the finer particles, beyond the resolution limit (around 10-30 nm) of AFM with a standard tip. This aggregation is a strong indication that PEG *bis(amine)* is chemically adsorbed onto the PMMA/SPIONs nanoparticles.

**Fig. 2 (D1, D2)** further illustrates in the morphology of the grafted nanoparticles after heavy metal (Co) chelation. The even larger domains of aggregation are observed, which ion-initiated formation of long chains and matrix is expected in the precipitation. This experimental result is in accordance with other reports [14-15, 18].



**Fig. 3.** FTIR spectra of (A) SPIONs, (B) SPIONs/PMMA, (C) SPIONs/PMMA-COOH and (D) PEG *bis(amine)* grafted PMMA/SPION.

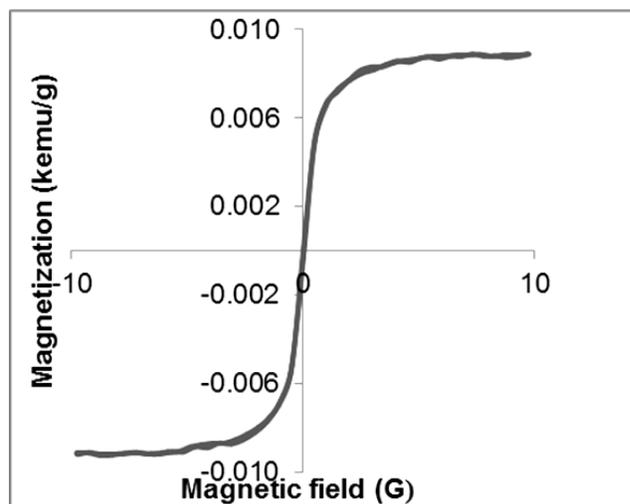
#### Fourier transforms infrared spectroscopy of modified PMMA/SPIONs

The different coating layers on the composite nanoparticles are confirmed by FTIR as shown in **Fig. 3**. The FTIR spectrum (**Fig. 3B**) of untreated SPIONs shows no significant peak while the characteristic peak of PMMA-coated SPIONs appears at  $1717\text{ cm}^{-1}$ , due to the vibration stretching from the ester carbonyl group. The two bands at  $2,942\text{ cm}^{-1}$  and  $2,830\text{ cm}^{-1}$  can be assigned to the C-H bond vibrations stretching from  $-\text{CH}_3$  and  $-\text{CH}_2-$  groups, respectively. From the above discussions, it can be concluded that the prepared polymer is indeed macromolecular PMMA.

In the FTIR spectra (**Fig. 3C**) of the SPIONs/PMMA-COOH, the broad band near  $3,400\text{ cm}^{-1}$  is the O-H bond in carboxyl group and the C=O stretching is around at  $1637-1700\text{ cm}^{-1}$  [18-20]. PEG *bis(amine)*-grafted on PMMA-SPIONs with amine containing  $-\text{NH}_2$  group and N-H bond yield peaks at  $3069\text{ cm}^{-1}$  and  $3276\text{ cm}^{-1}$ , respectively. Meanwhile, to the right of the amine peaks group, the

bending peaks of C=O and NH absorption are clearly observed at  $1621\text{ cm}^{-1}$  and at  $1527\text{ cm}^{-1}$ , respectively. These lead to a conclusion that the PEG *bis(amine)* is successfully grafted on SPIONs/PMMA.

Many research studies have focused on the interaction between the SPION cores and the polymer coating. For example, Morteza Mahmoudi *et al.*, reported that coating poly(ethylene glycol)-co-fumarate (PEGF) on iron oxide nanoparticles is highly reliable and easy to handle as magnetic nanoparticle are well dispersed [14]. They have confirmed that PEGF are chemically attached to SPIONs and control the bust effect of these particles. Bilsen Tural *et al.* has investigated the agglomeration of magnetic microparticles coated with poly methacrylic acid (PMAA) in an aqueous solution [21]. They found that weighted average sizes of magnetic microparticles with PMAA coated on surface increase from  $1.5\text{ }\mu\text{m}$  to  $3\text{ }\mu\text{m}$ . They believed that surfaces of microparticles are incompletely covered by PMAA. This may cause instability in the particle suspension and allows clustering to occur [21]. According to the interactive mechanism between the coating polymer and nanoparticles, based on the coating and modification of our study, we agree with previous contributors that PMMA has oxygen atoms in its polymer chain. These oxygen atoms have lone pair electrons, which can form coordination bond with Fe atoms. The interaction may not occur only between the lone pair electrons of PMMA atoms and Fe atoms, but also between the carbonyl group and Fe atoms. In addition, the interaction between carboxyl group and the amine group of PEG *bis(amine)* may lead to an internal salt called a zwitterion [21-23].



**Fig. 4.** Magnetization curve of grafted PEG *bis(amine)* on PMMA/SPION composite nanoparticles.

#### Magnetic property of composite nanoparticles

The magnetization behavior of PMMA/SPIONs composite nanoparticles grafted with PEG *bis(amine)* obtained by using VSM at room temperature is shown in **Fig. 4**.

Small remanent magnetizations are apparent, which is probably due to the aggregation of magnetic nanoparticles. The composite nanoparticles after coating and grafting pose the superparamagnetic property. The magnetization of the particles reaches the saturation magnetization of  $9.2\text{ kemu/g}$ .

### Heavy metal ions removal

The weight percentages of the heavy metal removal by the PEG *bis(amine)*-grafted PMMA/SPION composite nanoparticles are shown in Fig. 5. The results illustrate that seven kinds of heavy metal, including Cu(II), Mn(II), Zn(II), Cd(II), Pb(II), Co(II) and Ni(II) ions, can adsorb onto the nanoparticles and removed by an external magnet. The removal rates of Cu(II), Mn(II), Zn(II), Cd(II), Pb(II), Co(II) and Ni(II) are 80.0 %, 57.7 %, 54.3 %, 40.0 %, 34.8 %, 32.5 % and 30.3 % respectively. The results indicate that these heavy metal ions are possibly connected to the amine group on the surface of the composite nanoparticles. The chelation reactions depend on the concentration of metal ions, hydrogen ions and ligands. PEG *bis(amine)* on the surface of magnetic nanoparticles may exhibit varying degrees of protonation [25-26]. The NH<sub>2</sub> group is mainly responsible for interaction with anions on surface.

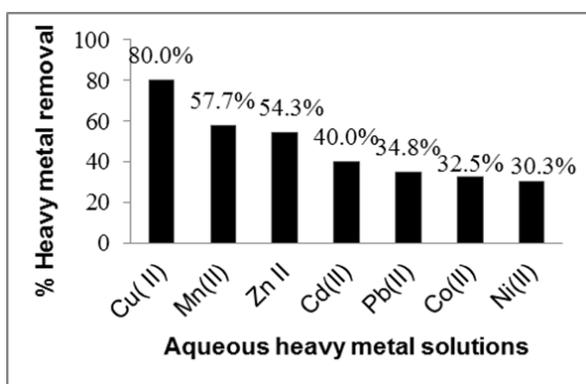


Fig. 5. Heavy metal ion removal for aqueous solutions by using PEG *bis(amine)*-grafted PMMA/SPION and an external magnetic field.

### Conclusion

In this paper, the synthesis of the PMMA/SPIONs composite magnetic nanoparticles grafted PEG *bis(amine)* are reported. The composite nanoparticles have been successfully prepared by an emulsion polymerization process in the aqueous suspension, followed by the hydrolysis functionalization with PEG *bis(amine)*. The capability of the grafted nanoparticles for heavy metal ion removal from aqueous solutions has been demonstrated. The selectivity of the composite nanoparticles to certain heavy metal ions should be further investigated. The synthesized nanoparticles have a potential use as nano-separators with high reliability and easy manipulation.

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