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Preparation and characterization of Zn(II) ion-imprinted polymer based on salicylic acrylate for recovery of Zn(II) ions

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Abstract

This work describes the synthesis of new ion-imprinted polymers (IIPs) for selective solid phase extraction of Zn(II) ions from aqueous samples. IIPs were synthesized by copolymerization of salicylic acrylate (SA) as a functional monomer and ethylene glycol dimethacrylate (EGDMA) as a crosslinker in the presence of 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The template ions were removed from IIPs particles by leaching with 0.1 M Ethylenediaminetetraacetic acid (EDTA) which leaves cavities in the particles with the capability of selective extraction of the Zn(II) ions. The monomer and the polymer after synthesis have been characterized by ^{1}H NMR, ^{13}C NMR and FT-IR studies. The effect of the pH on the extraction efficiency of Zn(II) ions was studied and optimized in pH around 6. The selectivity of the synthesized IIPs was studied in the presence of Co(II), Cd(II) and Ni(II) ions, and the IIPs showed higher affinity for Zn(II) in the presence of other interfering ions.

Keywords: *ion-imprinted polymers, salicylic acrylate, solid phase extraction, Zinc (II) ions.*

1. Introduction

Zinc is one of the most abundant elements in the Earth's crust. Zinc has many industrial applications includes; galvanizing iron, production of brass, zinc carbonate, zinc gluconate, zinc chloride, zinc pyrithionse and zinc sulfide. Also it is used as a negative plate for some batteries, roofing and gutters in building construction, as a coin material, die casting in the automobile industry. Also zinc oxide used in cosmetics and the production of white pigment[1].

Zinc is an essential mineral in human nutrition. Zinc involves in many of human metabolism pathways and it plays an important role in production of the genetic materials and cell division. Zinc exists in many foodstuffs with animal or plant sources. Deficiency of the zinc affects about two billion people in the world and cause many diseases. Also excess of zinc in the human body will lead to ataxia, lethargy and copper deficiency[2-5]. Furthermore, drinking water contains trace amounts of Zn(II) ions especially when stored in the metal containers. Industrial activities (such as mining, coal, waste combustion and steel processing) and toxic waste sites can increase the zinc pollution of the local water recourses to levels that may cause health problems. Thus extraction of the Zn(II) ions from complex matrix is very important for environmental and biological science[3-6].

Analysis and extraction of samples with complex matrix needs special attention in order to avoid matrix interferences beside preconcentration of the analytes and converting them into a more suitable form for the instrumental detection. The best solution for the complex sample analysis is the selective extraction of the interested analytes using sorbents with tailor-made recognition sites. Molecularly imprinted polymers (MIPs) provide this opportunity to synthesize very selective sorbents. MIPs are prepared in the presence of template molecules in order to mold template complementary binding sites[7-9]. MIPs can be synthesized by copolymerzation of a complex of a template and a functional monomer with a cross-linking agent in the environment of a porogenic solvent. After leaching the template molecules, a rigid three dimensional network remains with cavity complemented to the target compounds. MIPs showed many advantages such as high selectivity, easy preparation and low cost that makes them suitable candidate as a sorbent for the sample preparation of very complex samples. If the metal ions are used as templates for imprinting process, the resulting imprinted products are known as ion imprinted polymers (IIPs) that they can recognize metal ions with properties similar to the MIPs[10-14]. IIPs are selective and simple to synthesize. IIPs have been used for other application than solid phase extraction such as catalytic applications[15], chromatographic stationary phases[16], membrane separations[17] and sensors[18-20]. IIPs mainly used for the selective SPE of the trace metal pollutants from complex matrices[21-33]. This selective extraction and clean up cannot possible with the conventional sorbent.

Previously, for ion imprinting of zinc ions, following monomers have been used: styrene[26], methacrylic acid[23], 8-acryloyloxyquinoline[28], 4-vinylpyridine[24], 2-(diethylamino) ethyl methacrylate[22], 4-vinylpyridine[29]. While the following chelating agents have been used for the selective interaction with zinc ions: oxine[26], 3,5,7,20,40-pentahydroxyflavone[23], 2,2'-bipyridyl[24], 8-hydroxyquinoline[22], 2,2'-bipyridyl[29]. Salicylic acid has been extensively used for the extraction

of metal ions as a difunctional chelating reagent[34-37]. The chelating property of salicylate structure is due to the existence of an OH group in ortho position relative to the carboxyl or carbonyl group that can react with both hard and intermediate cations. Also salicylate moiety has been used as a chelating reagent in the structure of polymeric resins and has been used for metal ion extraction[38-43]. Furthermore, salicylic acid was used for functionalization of nanoparticles as a novel adsorbent and used for SPE of some heavy metal ions such as Cu(II), Cd(II), Ni(II) and Cr(III) ions[44]. Ion imprinted polymers based on the salicylate structure as chelating group has not been reported before. Salicylic acid was used in the preparation of a Cu-IIPs but in this work, only a carboxyl group of salicylic acid was available for complexation, while the main chelating agent was 4-(2-Pyridylazo) resorcinol[45]. Another similar work was a preparation of copper salicylate based MIPs for drug delivery purposes, that "copper salicylate" was the template molecule[46].

In this work, a new Zn(II)-ion imprinted polymer based on salicylic acrylate was synthesized and applied for the selective extraction and preconcentration of Zn(II) ions from aqueous solution. Salicylic acrylate as a chelating ligand was synthesized, characterized and its complexation with Zn(II) was studied. Zn(II)-salicylic acrylate complex monomer was synthesized and then polymerized with ethylene glycol dimethacrylate and AIBN as a crosslinking agent and initiator, respectively. The resulted product, (EGDMA-salicyl acrylate/Zn(II)) was characterized successfully. After removing the template Zn(II) ions from polymeric networks, the Zn(II)-IIPs have been achieved.

2. Materials and Methods

2.1 Materials

All of the reagents were of the highest purity and they used as received. Salicylaldehyde, ethylenediaminetetraacetic acid (EDTA) and ethylene glycol dimethacrylate (EGDMA) were purchased from Merck (Germany). Azobisisobutironitrile (AIBN) was achieved from Aldrich (St. Louis, MO, USA). Analytical grade zinc chloride dihydrate, cobalt acetate tetra hydrate, nickel sulfate hepta hydrate and cadmium nitrate tetra hydrate were obtained from Fluka (Buchs, Switzerland). Standard solutions of metal ions were prepared in the deionized water. All the other reagents and solvents were achieved from Merck and used as received.

2.2 Apparatus

All atomic measurements were carried out using a model Varian-200 flame atomic absorption spectrophotometer (Palo Alto, CA, USA) that equipped with a deuterium background correction system. Zinc absorbance was measured at 213.9 nm using spectral bandwidth (SBW) of 0.7 nm. For other element following condition was used, cobalt (λ: 240.0 nm, SBW: 0.2 nm), nickel (λ: 232.0, SBW: 0.2 nm) and cadmium (λ: 228.8 nm, SWB: 0.7 nm). Infrared spectra were recorded on a Perkin-Elmer-58B (Billerica, Massachusetts, USA) FT-IR spectrometer using KBr pellets in the range of 4000-200 cm^{-1}. The ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Advance DPX-250 MHZ. A model 713 Metrohm digital pH meter was used for pH adjustment.

2.3 Synthesis of salicylic acrylate

A 100 mL two necked round bottom flask was charged with salicylaldehyde (8 mmol), THF (12 mL), triethylamine (9.6 mmol). The flask was purged continuously with nitrogen gas and the reaction mixture was cooled in an ice-water bath (–5 °C). Then an amount of 9.6 mmol of acryloyl chloride (diluted in 1.5 mL THF) was added dropwise for 20 minutes with constant stirring in the ice-water bath. Then, the reaction mixture allowed achieving to the room temperature. After one hour the reaction was completed and the byproduct, quaternary ammonium salt, was filtered off. For purification purpose, the obtained product was dissolved in 5 mL dichloromethane and 5 mL of diluted acetic acid was added to the mixture. The organic phase was separated and the process repeated for three times. The solvent was evaporated in vacuum and the residue was dissolve in diethyl ether and petroleum ether. The mixture was heated at 60 °C to separate impurities, and after vacuum evaporation, a yellow oily purified product was achieved.

2.4 Synthesis of Zn(II) salicylic acrylate

The binary complex of Zn(II) salicylic acrylate was prepared by addition of an equal amount of salicylic acrylate and $ZnCl_2.2H_2O$ (0.26 mmol) to the 5 mL of chloroform–methanol mixture (3:2, v/v) under reflux condition with continuous stirring at 60 °C for 4 h. Solvent was evaporated and the residue was dissolved in diethyl ether and n-hexane, then the temperature was reduced to –5 °C. The complex was sedimented on the bottom of the flask.

2.5 Synthesis of Zn(II)-imprinted polymers

The Zn(II)-IIP was prepared by bulk polymerization. Salicylic acrylate (0.26 mmol) was added gently into the 5 mL of chloroform–methanol mixture (3:2, v/v) and then treated with $ZnCl_2.2H_2O$ (0.26 mmol) under reflex condition with continuous stirring at 60 °C for 4 hours. Afterward, EGDMA (2.6 mmol) and AIBN (6.5 mg) were added slowly to the mixture at room temperature. After 15 min stirring, the polymerization mixture was cooled to 0 °C while purging with N_2 and then heated at 60 °C for 18 hours. The resulting polymer was thoroughly washed with an appropriate amount of ethanol and dried at room temperature. The resultant polymer was dried at 70 °C for 24 h.

2.6 Leaching of Zn(II) ions from the Zn(II)-IIPs

The synthesized IIPs particles (0.2 g) were treated with 20 mL of 0.1 mol L-1 EDTA for 7 h at 60 °C. Then the solution was filtered and washed with 50 mL water. The washed solution analyzed by FAAS. The removal process was continued until no Zn(II) ion was detected.

2.7 Solid phase extraction of the metal ions

The ion imprinted polymer (40 mg) was equilibrated with 25 mL of metal ion solution (80 mg L^{-1}). The pH of the solution was adjusted between 2-7 using either ammonia or 1% acetic acid solution. Extraction was performed by

stirring the mixture for 1 h at room temperature. Finally, the solution was filtered and washed with 75 mL water and the concentration of Zn(II) ions in the resulting solution was measured by FAAS.

3. Results and Discussions

Salicylic acrylate ligand has appropriate functional groups (C=O and O-C=O) for complexation and polymerization. This oily mild yellowish ligand was synthesized successfully and purified by liquid-liquid extraction using diethyl ether and n-hexane as solvent with recovery percentages higher than 89%. The product structure was characterized and confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectra. A scheme for the synthesis procedure is shown in Figure 1.

3.1 FT-IR study of salicylic acrylate

The successful synthesis of salicylic acrylate is demonstrated by the FT-IR spectrum in Figure 2. Two characteristic absorption bands in 1740 cm^{-1} and 1695 cm^{-1}, are related to the C=O group of both ester and aldehyde. Furthermore, other bands at 1603 cm^{-1} and 2815 cm^{-1} are corresponded to the C=C group and stretching vibrations of C-H bond of the aldehyde. Bands around 1410 cm^{-1} and 1455 cm^{-1} are attributed to aromatic C-C stretching vibrations and 1135 cm^{-1} and 1155 cm^{-1} are related to C-O strong stretching.

3.2 ^{1}H NMR study of salicylic acrylate

The ^{1}H NMR spectrum of salicylic acrylate (Figure 3) indicates eight signals. There are two doublets at chemical shift of 6, 6.6 and a quartet at 6.4 ppm that pertain to the methylene and methyne group, respectively. Signals in the chemical shift of 7.1-7.9 ppm belong to the hydrogen's of the aromatic rings. A singlet signal in the chemical shift of 10.1 ppm refers to the aldehydic hydrogen. Lack of alcoholic signal at 5.2 ppm demonstrated the evolution of the reaction.

3.3 ^{13}C NMR study of salicylic acrylate

The ^{13}C NMR spectrum of the salicylic acrylate ligand in the $CDCl_3$ is shown in Figure 4. There are ten different chemical shift signals in the range of 123-188 ppm. The significant signals at 127 and 133 ppm belong to the carbons of the

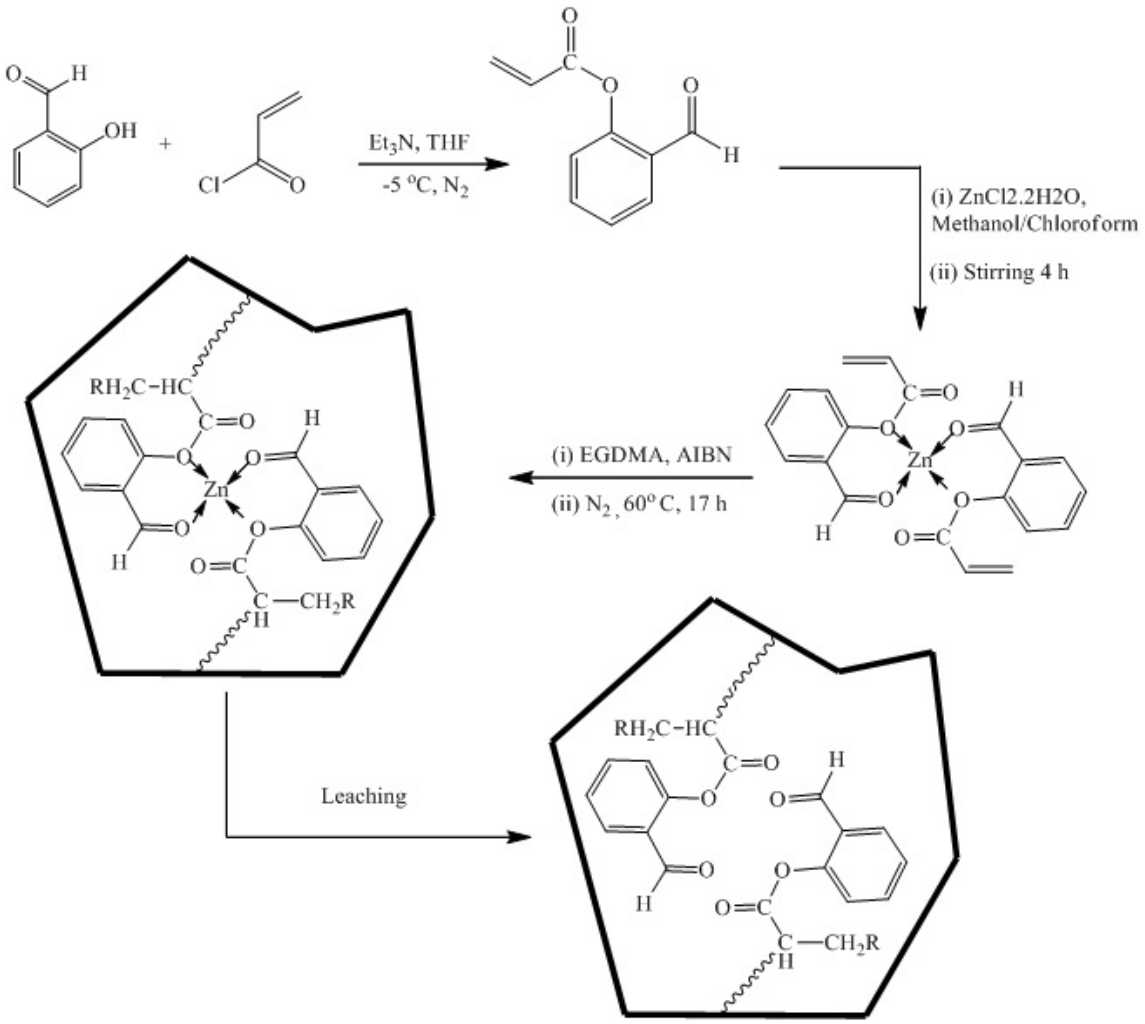

Figure 1. Scheme for preparation of Zn(II) ion-imprinted polymer.

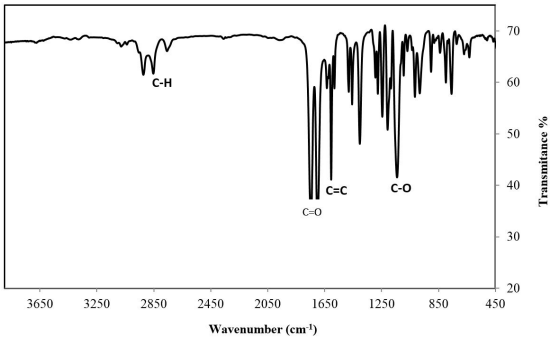

Figure 2. The FT-IR spectra of salicylic acrylate.

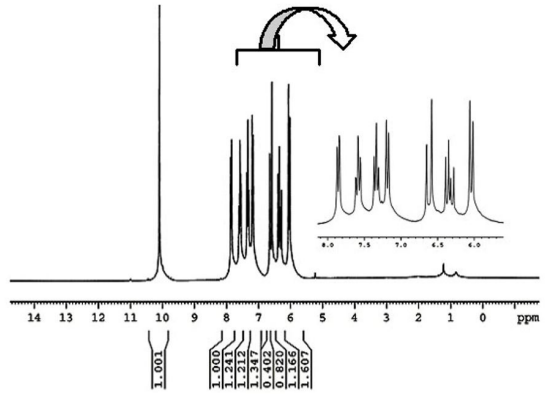

Figure 3. ^{1}H NMR spectrum of salicylic acrylate in $CDCl_3$.

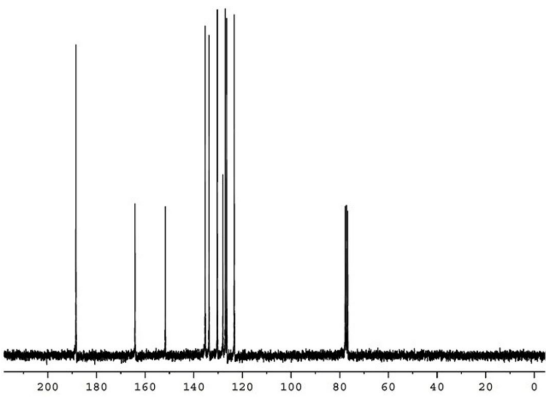

Figure 4. ^{13}C NMR spectrum of salicylic acrylate in $CDCl_3$.

olefin group, indicating alpha and beta carbon near to the carbonyl group, respectively. The signals in the region of 128 and 151 ppm are related to the ipso carbon of the ring connected to the aldehyde and ester groups, respectively. Other carbons of the aromatic ring are located in the chemical shifts of 123, 126, 130 and 135 ppm. The chemical shifts at 164 and 188 ppm indicate the carbons of the ester and aldehyde groups.

3.4 FT-IR study of Zn(II) salicylic acrylate complex

The FT-IR spectra of the ligand, Zn(II) ions and complex were superimposed in Figure 5 for comparison. There are some partial difference between the ligand and the complex

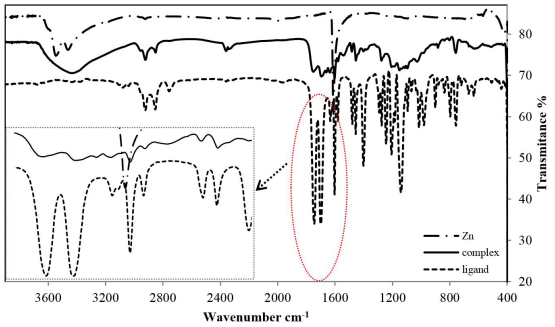

Figure 5. The comparison of the FT-IR spectra of the Zn, ligand and complex.

spectra. Peak at 753 cm^{-1} are attributed to ortho substituted aromatic ring. The carbonyl peaks of aldehyde and ester group for the complex are located at 1690 cm^{-1} and 1731 cm^{-1}, respectively. These peaks have around 10 cm^{-1} shift toward lower wavenumber relative to the ligand. That is due to the rigid structure of the complex that reduces vibration of the atoms in the complex structure and leads to lower peak intensities. The weak stretching vibration of the aldehyde at the region of 2726 cm^{-1} in the complex spectra was vanished due of the contribution of the carbonyl group in the complexation with metal ions.

3.5 UV-Vis spectra of ligand and complex

The complexation of the salicylic acrylate with Zn(II) ions can be observed in UV-Vis spectra (Figure 6). Strong peak at 200 cm^{-1} are related to the aromatic ring $\pi \rightarrow \pi^*$ translation is common for both ligand and complex. Peak at 250 cm^{-1} are carbonyl $\pi \rightarrow \pi^*$ translation with 15 cm^{-1} relocation. Peak at 280 cm^{-1} is a forbidden $n \rightarrow \pi^*$ translation of carbonyl group that disappeared in the complex spectrum due to involving nonbonding electron pair in complexion with a Zn(II) ion. The electronic absorption spectra of the complex show a weak shoulder peak in the region of 415-445 nm which are assigned to the spin allowed metal-to-ligand charge transfer (MLCT) $d \rightarrow \pi^*$ transition.

3.6 Preparation and ^{1}H NMR study of polymer

Copolymer of imprinted poly (EGDMA/salicylic acrylate/Zn(II)) was performed by in situ polymerization in aqueous solution. The prepared polymer has an Indian red color and characterized by FT-IR and ^{1}H NMR. The polymerization occurs by free radical polymerization mechanism, in which initiator molecule (AIBN) produces radical upon heating at 60 °C. The reaction continues to produce stable type III radical in EGDMA that processes to polymer synthesis. The ^{1}H NMR spectrum of poly (EGDMA/salicylic acrylate/Zn(II)) particles is shown in Figure 7. According to this spectrum the peaks corresponding to the ligand and also EGDMA are completely detectable. The signal in the chemical shift of 10.1 ppm is attributed to the aldehydic hydrogen of salicylic acrylate. The hydrogens of aromatic ring are indicated in chemical shift of 7-7.8 ppm. In a broad area of 1.2-2.2 ppm the aliphatic hydrogens of ligand and crosslinker in polymer network are observable. The signals in the regions of 4.3, 5.6 and 6.2 ppm are related to EGDMA.

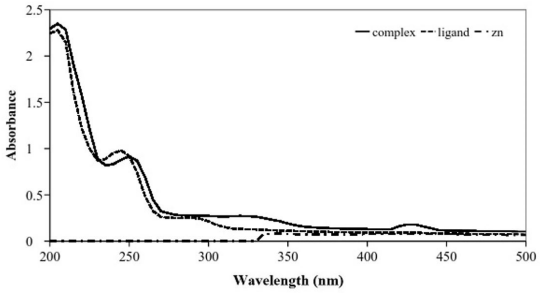

Figure 6. The comparison of the UV-Vis spectra of the Zn, ligand and complex.

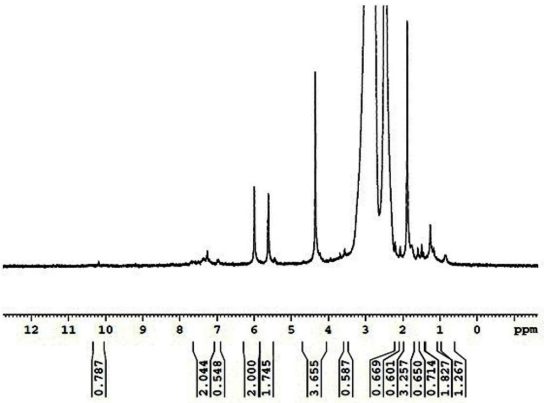

Figure 7. ^{1}H NMR spectrum of poly (EGDMA/salicylic acrylate/ Zn(II)) in DMSO.

3.7 Solid phase extraction and pH optimization

The extraction efficiency of the IIP particles was investigated by batch extraction of the Zn(II) ions from aqueous solution. Before the extraction process, the polymer particles completely leached using 0.1 M EDTA solution and then applied for batch solid phase extractions. The most important parameter effective in the extraction efficiency of the IIPs was studied at different pH value in the range of 2-7. The percent of the extraction is shown in the Figure 8. By increasing the pH, the amount of the extraction increased until pH 5.75 and reached to its maximum amount around 97.88% and then reduced slightly due to increased OH^- and consequent $Zn(OH)_2$ precipitation.

3.8 Selectivity of the Zn(II)-IIPs

Competitive adsorption of zinc ions in the presence of disturbing ions such as Cd(II), Ni(II) and Co(II) was also investigated and the results are shown in Table 1. Although these ions possess a similar ionic radii (Zn(II) = 74 pm, Cd(II) = 71 pm, Ni(II) = 69 pm and Co(II) = 72 pm)[47], the competitive adsorption of Zn(II) ions on the prepared Zn(II)-IIPs in the presence of other metal ions, showed a higher amount of absorption selectivity. It is interesting to compare the selectivity of the prepared Zn(II)-IIPs with a resin prepared by salicylic acid, hexamethylene diamine and formaldehyde in which the salicylate moiety act as a chelating group[48]. This resin for a series of ions showed

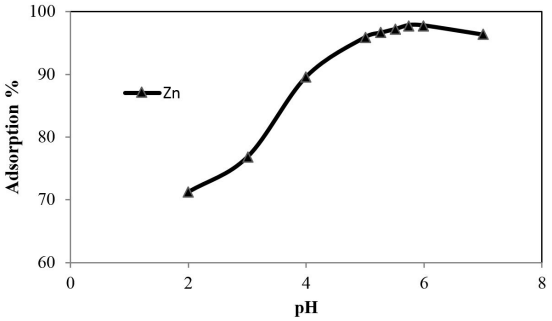

Figure 8. Effect of pH on the extraction of Zn(II) ions using the Zn(II)-IIPs.

Table 1. Selectivity experiments in the presence of disturbing ions. The concentration of all metal ions was equal to 80 mg L^{-1}.

Cation/ pH	Extraction efficiency (%)					
	2	3	4	5	6	7
Zn(II)	60.1	66.5	81.7	90.6	94.9	90.8
Co(II)	5.7	10.2	17.7	28.2	35.5	29.3
Ni(II)	3.0	6.2	7.5	17.1	10.5	6.8
Cd(II)	4.6	6.4	2.0	12.2	19.9	27.6

following order of selectivity: Fe(III) > Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II) > Pb(II), while the same functional group in the current work showed very high selectivity for Zn(II) among Zn(II), Co(II) and Ni(II). This superiority is attributed to Zn(II) ion recognition sites imprinted in the polymer.

4. Conclusions

In this study an ion imprinted polymer selective for Zn(II) ions was synthesized by copolymerization of salicylic acrylate and cross linking agent EGDMA in the presence of AIBN as initiator and its application for solid phase extraction of the metal ions was investigated. The maximum amount of adsorption of Zn(II) ion was obtained at pH 5.75 equal to 98 percent. The competitive adsorption experiments showed superiority of prepared IIPs toward Zn(II) ion even in the presence of Cd(II), Ni(II) and Co(II) ions which have the similar ionic radius.

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