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Synthesis and characterization of novel ion-imprinted polymeric nanoparticles for very fast and highly selective recognition of copper(II) ions

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ABSTRACT

This work reports the preparation of new Cu^{2+} ion-imprinted polymeric nanoparticles using 1-hydroxy-4-(prop-2′-enyloxy)-9,10-anthraquinone (AQ) as a vinylated chelating agent. The Cu^{2+} ion found to form a stable 1:1 complex with AQ in methanol solution. The resulting Cu^{2+}–AQ complex was copolymerized with ethyleneglycol dimethacrylate, as a cross-linking monomer, via precipitation polymerization method. The imprint copper ion was removed from the polymeric matrix using a 0.1 mol L^{-1} HNO_3 solution. The Cu^{2+}-imprinted polymeric nanoparticles were characterized by IR spectroscopy, scanning electron microscopy (SEM) and N_2 adsorption–desorption isotherms. The SEM micrographs showed colloidal nanoparticles of 60–100 nm in diameter and slightly irregular in shape. Optimum pH for maximum sorption was 7.0. Sorption and desorption of Cu^{2+} ion on the IIP nanoparticles were quite fast and achieved completely over entire investigated time periods of 2–30 min. Maximum sorbent capacity and enrichment factor of the prepared IIP for Cu^{2+} were 73.8 μmol g^{-1} and 56.5, respectively. The relative standard deviation and limit of detection ($C_{LOD} = 3S_b/m$) of the method were evaluated as 2.6% and 0.1 ng mL^{-1}, using inductively coupled plasma-atomic emission spectrometry, respectively. It was found that the imprinting technology results in increased affinity of the prepared material toward Cu^{2+} ion over other metal ions with the same charge and close ionic radius. The relative standard deviations for six and twenty replicates with the same nanoparticles were found to be 1.7% and 2.1%, respectively.

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1. Introduction

Ion-imprinted polymeric materials containing metal ion recognition sites are synthesized via copolymerization with functional and cross-linking monomers in the presence of at least one imprint metal ion in the form of complex with a suitable ligand. The polymerization is usually carried out by radiochemical (γ-irradiation) method [1], in the absence of initiator, or by photochemical (UV irradiation) [2] and thermal [3] methods, in the presence of an initiator. There are several methods for the synthesis of ion imprinted polymers, including bulk [4,5], precipitation [5], dispersion or suspension [5] and surface imprinting [2,6] polymerization methods. In some methods, the synthesized polymers are in the form of blocks and, in others, are in the form of particles. In the former case, the block materials are ground and sieved after drying to obtain metal ion-imprinted polymeric particles. In all cases, the imprint metal ion is removed from the polymeric particles by leaching with a mineral acid which leaves cavities or “imprinted sites” in the polymeric particles that are complementary in shape and size of the imprint metal ion. The prepared polymers can be characterized using IR spectroscopy, scanning electron microscopy (SEM) and N_2 adsorption–desorption isotherms. The resultant polymeric particles can be used as extractants for selective separation and enrichment of the imprint metal ion from dilute aqueous solutions by batch or column experiments.

Imprint metal ions have the ability to bind to functional groups through the donation of electrons from the heteroatoms of ligands and functional monomers to the unfilled orbitals of their outer coordination sphere. The strength of interaction can vary enormously from weak and readily exchangeable bonds to strong bonds, which behave like covalent links, depending on the nature of imprint metal ion, its oxidation state and ligand characteristics [7]. The selectivity of ion-imprinted polymers increases with increasing strength of the interaction between imprint ion and heteroatoms of the ligands and functional monomers before polymerization process.

In recent years, the ion-imprinted polymers have found interesting applications in solid phase extractions [8], sensors [9] and

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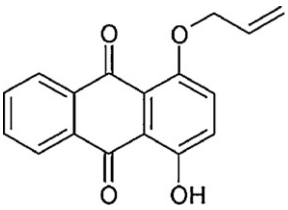

Scheme 1. Structure of 1-hydroxy-4-(prop-2′-enyloxy)-9,10-anthraquinone (AQ).

membrane separations of imprint metal ions [6]. Several recent published papers have reported the synthesis of IIP materials and their use in separation of transition [6,10–23], lanthanide [1,8,24–27] and actinide [3,28–31] metal ions.

A great variety of analytical procedures for copper(II) enrichment have been proposed, mainly based on liquid–liquid extraction [32,33], co-precipitation [34], solid phase extraction (SPE) [35,36] and cloud point extraction [37,38]. In comparison with the other solid phase extraction methods, especially the ion exchange resins, the imprinting method is quite simple and easy to perform in a tailor-made fashion [39]. To prepare a receptor for a certain guest metal ion, appropriate monomers can be simply polymerized in the presence of the guest compound as a template [1,3,6,8–10,24,28]. Actually, the functional monomers can be selected according to the nature of template ion. Similar to ion exchangers and due to basic or acidic functional groups in binding sites, sorption of compound could be affected by solution pH [9,39]. Predefined cavities on imprinted polymers may lead to greater selectivities than ion exchangers at appropriate conditions [39]. However, in spite of the availability of the traditional ion exchangers, the ion-imprinted sorbents are on the horizon; this methodology certainly opens the way to further developments in science and technology.

Due to biological and environmental impact of copper ion, the development of new methods for selective separation, purification and determination of Cu^{2+} is of increasing interest. There are a number of previously published papers dealing with the preparation of ion selective imprinted polymers for copper(II) ion [4,10–14,20–23].

9,10-Anthraquinone derivatives, as the largest group of naturally occurring quinones, are of fundamental importance both in industry [40,41] and in medicine [42,43]. To the best of our knowledge, there is no previous literature report on the use of 1-hydroxy-4-(prop-2′-enyloxy)-9,10-anthraquinone (AQ, Scheme 1) in the preparation of Cu^{2+}-imprinted polymeric nanoparticles for the very fast sorption/desorption of Cu^{2+} ions in aqueous solutions. In this paper, we report the synthesis of novel ion-imprinted polymeric nanoparticles using AQ as a vinylated chelating agent for selective separation and enrichment of imprint Cu^{2+} ions in aqueous solutions. The IIP was synthesized via precipitation copolymerization of Cu^{2+}–AQ complex with ethyleneglycol dimethacrylate as a cross-linker monomer in the presence of 2,2′-azobis(isobutyronitrile) as a radical initiator for the preparation of effective binding sites in polymeric network. Characterization of the synthesized material and its sorption and desorption behavior after removal of copper(II) ions are described and discussed.

2. Experimental

2.1. Chemicals

Ethyleneglycol dimethacrylate (EGDMA) was supplied by Merck (Darmstadt, Germany). 2,2′-Azobis(isobutyronitrile) (AIBN) was obtained from Aldrich (St. Louis, MO, USA). 1-Hydroxy-4-(prop-2′-enyloxy)-9,10-anthraquinone (AQ) was synthesized and purified as described elsewhere [44]. Analytical grade $Cu(NO_{3d})_2{\cdot}3H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Mn(NO_3)_2{\cdot}4H_2O$, $NaH_2PO_4{\cdot}2H_2O$, NaOH and HNO_3 were purchased from Merck. Solutions of metal ions were prepared in doubly distilled water. All solvents used (i.e., acetonitrile, methanol and acetone) were of reagent grade and obtained from Merck. Solutions of pH 2–8 were prepared by adding NaOH or HNO_3 to NaH_2PO_4 solutions.

2.2. Apparatus

A Varian Vista Pro (CCD simultaneous) model inductively coupled plasma (Palo Alto, CA, USA) was used for the determination of all metal ions. The operational conditions for ICP AES and wavelength of analytical lines were in accordance with manufacturer's instructions. The wavelengths used were as follows: Cu 324.754 nm, Co 238.892 nm, Ni 231.604 nm, Zn 213.9 nm, and Mn 228.802 nm. The IR spectra (4000–500 cm^{-1}) were recorded on a 460 model IR spectrometer (Shimadzu, Kyoto, Japan) after drying of polymeric nanoparticles at 80 °C for 5 h. A model 713 digital pH meter (Metrohm, Germany) was used for pH adjustments. Elemental analyses (EA) were performed on a Vario El III CHN analyzer (Elementar, Hanau, Germany). All absorption spectra were recorded on a UV-visible spectrophotometer (S-2100 series, SCINCO Co. Ltd., Korea), equipped with a thermostated cell compartment. A Frigomix thermostat (Compiegne, France) was used to keep the solution temperature constant at 25.00 ± 0.05 °C. Scanning electron micrographs were obtained on a model XL30 scanning electron microscope (Philips, Holland). The N_2 adsorption–desorption isotherms were recorded on a NOVA 2000e surface area and pore size analyzer (Quantachrome, USA) at 77 K.

2.3. Preparation of ion-imprinted polymeric nanoparticles

The copper(II) ion-imprinted nanoparticles were prepared by thermal precipitation polymerization technique. The procedure for synthesis of poly(EGDMA–AQ/Cu(II)) nanoparticles was achieved in two steps. In the first step, the complexation was attained by allowing 1-hydroxy-4-(prop-2′-enyloxy)-9,10-anthraquinone (AQ, 1 mmol), as vinylated ligand, and $Cu(NO_3)_2{\cdot}3H_2O$ (1 mmol), as imprint metal ion (template), respectively, to interact with each other in acetonitrile (45 mL) as a polymerization solvent in a 100 mL vial to produce Cu^{2+}–AQ complex for the next step. The formation of a red complex was confirmed spectrophotometrically. In the second step, EGDMA (20 mmol) and AIBN (0.4 mmol) were added as a cross-linker and a free radical initiator, respectively, to the first step solution and stirred at room temperature. Argon gas was bubbled trough the prepolymerization mixture for 5 min to remove molecular oxygen from it, since it traps the radicals and retards the polymerization.

Then the reaction vial was sealed and heated in an oil bath at 60 °C for 24 h under magnetic stirring at 400 rpm to complete the thermal polymerization. After polymerization, the excess amount of solvent was removed by centrifugation of the resulting suspension solution. The prepared polymer was washed several times with 1:4 (v/v) methanol/water to remove the unreacted materials and then with 0.1 mol L^{-1} HNO_3 for leaching of the imprint metal ions until the wash solution was free from Cu^{2+} ions. Finally, it was washed with double distilled water until a neutral pH is reached. The resulting fine yellow powder was dried overnight before sorption and desorption studies. The synthesis of non-imprinted polymer (NIP, poly(EGDMA–AQ)) was carried out similar to that of the Cu(II)-IIP, but in the absence of any $Cu(NO_3)_2{\cdot}3H_2O$ salt as template, and dried at 80 °C for 2 h.

2.4. Sorption and desorption procedure

The sorption and desorption studies of the Cu^{2+} ions on the prepared imprinted polymer were carried out by batch experiments as follows. An aliquot of Cu^{2+} solution (e.g., 10 mL of 1 μg mL^{-1}) was treated with 30 mg of polymeric nanoparticles at the desired pH, using a suitable phosphate buffer. The suspension was stirred for pre-selected periods of time using a magnetic stirrer. After centrifugation (5 min, 6000 rpm), the supernatant solution was removed. Then, the Cu^{2+} ions preconcentrated onto the IIP nanoparticles were eluted using 5 mL of 0.1 mol L^{-1} HNO_3, after stirring for 5 min. The suspension was then centrifuged and the eluent solution containing copper ions was removed from the nanoparticles. Finally, the resulted solution was used for determining its copper content by ICP AES.

The percentage of metal ion extracted into the sorbent was determined by comparing its concentrations before, C_i (μg mL^{-1}), and after extraction, C_e (μg mL^{-1}), as [12]:

$$\%E = \frac{(C_i - C_e)}{C_i} \times 100 \tag{1}$$

The sorption capacity (μmol g^{-1}) of the IIP nanoparticles relative to the imprint metal ion was calculated by:

$$Q = \frac{(C_i - C_e)V}{mM} \tag{2}$$

where V is the volume of initial solution (mL), m is the mass of IIP materials (g), and M is the atomic mass of copper (g mol^{-1}).

The distribution ratio (K_d, mL g^{-1}) of Cu^{2+} ions between the IIP nanoparticles and aqueous solution was also determined by following equation:

$$K_d = \frac{(C_i - C_e)V}{C_e m} \tag{3}$$

Selectivity coefficients for copper(II) ion relative to foreign ions are defined as:

$$k_{Cu^{2+}/M^{n+}} = \frac{K_d^{Cu^{2+}}}{K_d^{M^{n+}}} \tag{4}$$

where $K_d^{Cu^{2+}}$ and $K_d^{M^{n+}}$ are distribution ratios of copper and foreign ion, respectively. The relative selectively coefficient, k', is defined as:

$$k' = \frac{k_{\text{imprinted}}}{k_{\text{non-imprinted}}} \tag{5}$$

where $k_{\text{imprinted}}$ and $k_{\text{non-imprinted}}$ are selectivity coefficients of the imprinted and non-imprinted nanoparticles, respectively. The relative selectively coefficient allows an estimation of the effect of imprinting on selectivity [12].

3. Results and discussion

Although one of the most established procedures for the preparation of effective ion-imprinted polymers is trapping of non-vinylated chelating agents in polymeric matrices [9], the preparation of IIPs via covalent binding of vinylated chelating agents in polymeric matrices is of special interest. In this method, the vinylated ligand–metal ion (host–guest) complex is copolymerized with a cross-linking agent, which provides spatially regulated sites in the polymer matrix. In this paper, we synthesized novel ion-imprinted polymeric nanoparticles based on the employment of 1-hydroxy-4-(prop-2′-enyloxy)-9,10-anthraquinone (AQ) as a suitable vinylated chelating agent for selective separation and enrichment of imprint Cu^{2+} ions using EGDMA as a cross-linker monomer in aqueous solutions.

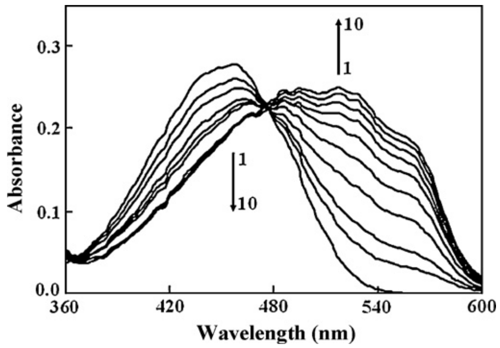

Fig. 1. Visible spectra of a 5.0×10^{-5} mol L^{-1} solution of AQ ligand obtained upon titration with a 5.0×10^{-3} mol L^{-1} solution of Cu^{2+} ion in methanol at 25.00 ± 0.05 °C. The [Cu^{2+}]/[AQ] mole ratios are: (1) 0.0, (2) 0.2, (3) 0.4, (4) 0.6, (5) 0.8, (6) 1.0, (7) 2.0, (8) 2.6, (9) 3.0, and (10) 3.6.

3.1. Preliminary complexation studies

In order to obtain some information about the stoichiometry and stability of the AQ complex with copper ion in methanol solution, the absorbance of a 5.0×10^{-5} mol L^{-1} ligand (AQ) solution was monitored as a function of metal ion/ligand molar ratios during its titration with a 5.0×10^{-3} mol L^{-1} of Cu^{2+} ion in the same solvent at 25.00 ± 0.05 °C (Fig. 1). As it is seen from Fig. 1, the complexation is accompanied by a relatively strong shift of the absorption band of AQ, with a λ_{max} of 456 nm in methanol solution, toward longer wavelengths (i.e., λ_{max} = 516 nm). Generally, the electrostatic interaction of a bound metal ion would not be able to produce such pronounced effects on the electronic structure of a dye molecule, and hence its spectrum [45]. It seems reasonable that a large change in the conjugation of AQ molecule, brought about upon copper ion complexation, is responsible for the observed spectral changes [46].

The resulting molar ratio plots, obtained from the corresponding spectra during the titration process (Fig. 1), at both 456 and 516 nm are shown in Fig. 2. As is obvious from Fig. 2, both molar ratio plots show a relatively sharp inflection point at a [Cu^{2+}]/[AQ] molar ratio of about 1, emphasizing the formation of a 1:1 ligand to metal complex in solution. The existence of a well-defined isosbestic point in the spectra of AQ titration with copper ion (Fig. 1) is also a good indication for occurrence of a simple 1:1 complexation equilibrium in solution [45,46]. The complex formation constant K_f was evaluated by computer fitting of the mole ratio data to an appropriate equation [47] using a non-linear least-squares program KINFIT [48]. The resulting log K_f was found to be 5.09 ± 0.07.

The stoichiometry of the complex was also confirmed by the continuous variations method [49]. The resulting symmetrical continuous variations plot obtained at 556 nm are shown in Fig. 3. The

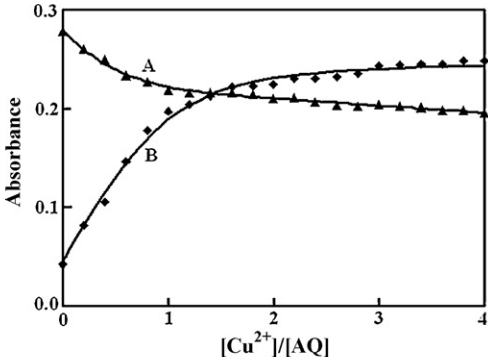

Fig. 2. Absorbance–mole ratio plots for Cu^{2+}–AQ system in methanol solution at (A) 456 nm, (B) 516 nm and (—) fitted line.

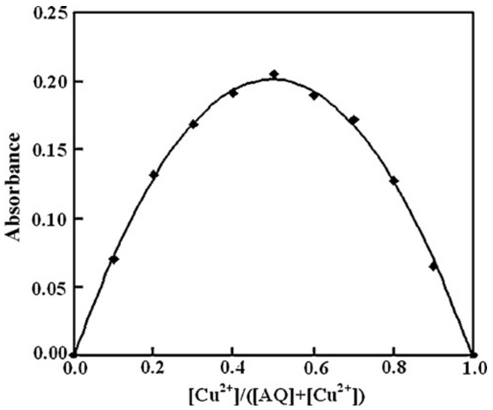

Fig. 3. Continuous variations plot for Cu^{2+}–AQ system in methanol solution at 556 nm, total concentration, 1.0×10^{-4} M.

observation of the maximum absorbance at a $[Cu^{2+}]/([AQ]+[Cu^{2+}])$ ratio of 0.5 clearly indicates the formation of a 1:1 complex between Cu^{2+} and AQ in solution. A schematic representation for the preparation of the Cu^{2+}–IIP and its role in the sorption and desorption process of the Cu^{2+} ions is shown in Fig. 4.

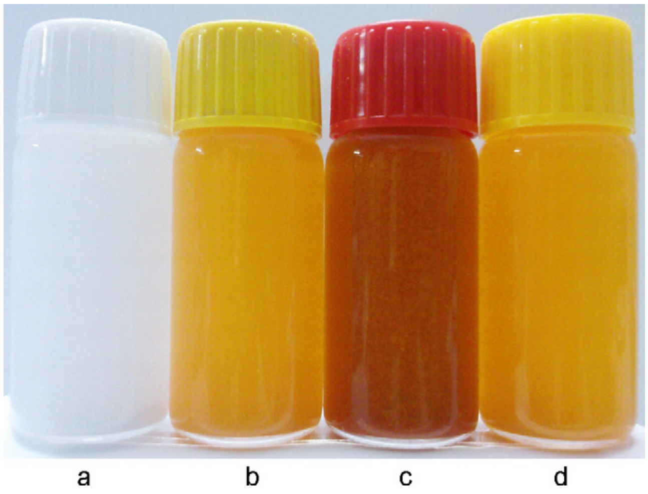

Fig. 5. Photographs of the suspended polymers. (a) poly(EGDMA) (b) poly(EGDMA–AQ), NIP (c) poly(EGDMA–AQ/Cu(II)), unleached IIP (d) poly(EGDMA–AQ/imprinted site), leached IIP. The polymers (a), (b) and (c) are suspended in a buffer solution pH 7.0 and (d) is suspended in a buffer solution pH 7.0 containing Cu^{2+} ion after its sorption on the polymer and (d) is suspended in a 0.1 mol L^{-1} HNO_3 solution after desorption the Cu^{2+} ions from the polymer.

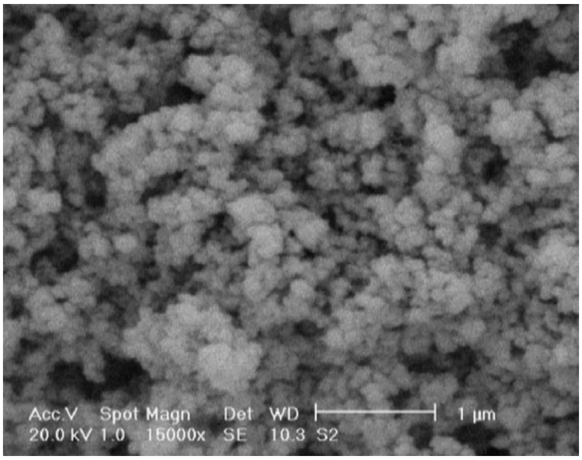

Fig. 6. Scanning electron micrograph of the Cu^{2+}-imprinted polymeric nanoparticles obtained via precipitation polymerization method.

3.2. Characterization of IIP

The resulting imprinted nanoparticles obtained from copolymerization of the Cu^{2+}–AQ complex with EGDMA, as a cross-linking monomer, via precipitation polymerization method (Fig. 4) were characterized by IR spectroscopy, colorimetry, scanning electron microscopy, elemental analysis and N_2 adsorption–desorption isotherms.

In the IR spectra, the absorptions due to carbonyl group (1729 cm^{-1}), C–O stretch (1156, 1247 cm^{-1}), C–H stretch (2990 cm^{-1}), CH_3 and CH_2 bends (1383 and 1452 cm^{-1}, respectively) were observed. It is interesting to note that no band is present in the region of 1630–1645 cm^{-1} indicating the absence of C=C groups in polymer materials. This confirms the complete copolymerization of the vinylated AQ ligand and EGDMA.

As is quite obvious from Fig. 5, the different colors of the non-imprinted polymers prepared in the absence (a, poly(EGDMA), white) and presence (b, poly(EGDMA–AQ), yellow) of vinylated ligand AQ clearly indicated the presence of AQ ligand in the matrix of NIP. While the red color of the imprinted polymer, poly(EGDMA–AQ/Cu(II) (c) is an obvious indication for the presence of the template ion as a Cu^{2+}–AQ complex in the polymeric matrix. Moreover, a further change in color from red (c) to yellow (d) is a clear result of desorption of the Cu^{2+} ions from the IIP nanoparticles upon its washing with a 0.1 mol L^{-1} HNO_3 solution.

The morphology of the Cu^{2+}-IIP produced by the precipitation method was assessed by scanning electron microscopy, and the SEM patterns are shown in Fig. 6. As seen, the precipitation polymerization resulted in colloidal nanoparticles of 60–100 nm in diameter which are slightly irregular in shape. In this type of polymerization, it has been suggested that the morphology of the individual particles can be improved by varying the stirring speed of polymerization solution during the synthesis of the polymer [5].

To evaluate the degree of AQ incorporation, the IIP nanoparticles were subjected to elemental analysis after washing by double distilled water for removing of Cu^{2+}, H^+ and $NO_3{}^-$ ions from polymer network followed by drying at 80 °C for 5 h. The results of EA of acid leached IIPs were found to be: %calculated (%found); C, 61.03 (59.55%); H, 7.02% (6.99%); O, 31.95% (33.46%). It should be noted that the calculated results for the elemental analysis were based on

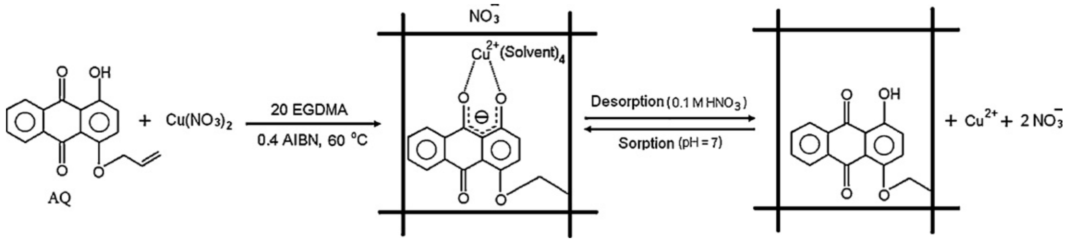

Fig. 4. Schematic representation of the synthesis of the Cu^{2+}-imprinted polymer and its role in the sorption and desorption process of the Cu^{2+} ions.

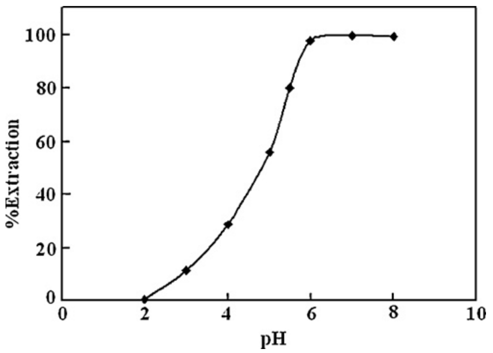

Fig. 7. Effect of pH on sorption of copper(II) ions on imprinted polymeric nanoparticles.

the assumption of complete monomer conversion and almost 50% AQ entrapment, as discussed above. Meanwhile, the EA results for a non AQ-containing polymer (white color polymer) were found to be: %calculated (%found); C, 60.61% (60.54%); H, 7.11% (7.15%); O, 32.28% (32.31%).

The synthesized IIP nanoparticles were also characterized using nitrogen adsorption–desorption studies, in order to obtain some information about the surface area, pore volume and average pore diameter of the leached polymer material. The surface area was determined by applying the Brunauer–Emmett–Teller (BET) theory whereas the pore volume and average pore diameter were derived by the Barrett–Joyner–Halenda (BJH) theory. The multipoint BET surface area, BJH adsorption cumulative pore volume and BJH adsorption average pore diameter of the prepared Cu^{2+}-imprinted polymer were found to be $16.82\,m^2\,g^{-1}$, $0.0218\,cm^3\,g^{-1}$ and 1.94 nm, respectively, indicating that polymer materials with nanopores have been prepared in the present study.

3.3. *Sorption studies*

3.3.1. *Effect of pH*

In the absence of chelating agents, the hydrolysis of copper ion is affected by the total concentration of soluble metal species and pH of the medium [12,13,50,51]. In order to prevent the precipitation of copper hydroxide at alkaline conditions during the variation of pH, we employed a low copper concentration of $1\,\mu g\,mL^{-1}$. The effect of pH on the sorption of Cu^{2+} ions was then investigated by varying the solution pH from 2.0 to 8.0. Several batch experiments were performed by equilibrating 30 mg of the imprinted nanoparticles with 10 mL of solutions containing $1\,\mu g\,mL^{-1}$ of Cu^{2+} under the desired range of pH and a sorption time of 5 min. The pH dependence of extracted percentage of Cu^{2+} is shown in Fig. 7. As seen, the binding of Cu^{2+} ions increased with increasing pH and reached to maximum at pH 7.0. As expected, due to the involvement of the hydroxylate group of AQ in complexation with Cu^{2+} ion [52], the copper ion sorption at lower pH values are highly dependent on the pH of solution, because of the competition of proton with copper ion for hydroxylate site of AQ, so that smaller amounts of copper ions are adsorbed by the polymer. As the pH increased, the protonation of ligand is suppressed and condition becomes more favorable for complex formation and sorption of Cu^{2+} ions to the imprinted sorbent. As is obvious from Fig. 7, the extraction of copper ions by the sorbent becomes quantitative at pH 7.0 and remains constant up to pH 8.0. The pH above 8.0 was not investigated because of the possibility of hydrolysis and precipitation of the copper ions.

3.3.2. *Effect of sample volume*

In the analysis of real samples, the sample volume is one of the important parameters influencing the preconcentration factor. Therefore, the effect of the sample volume on the quantitative adsorption of Cu^{2+} ion was investigated. For this purpose, 50, 100, 200, 300, 400, and 500 mL of sample solutions containing a constant amount of Cu^{2+} ion (i.e., $10\,\mu g$) were equilibrated with 30 mg of the sorbent in several batch procedures. The pH of solutions was adjusted at 7.0 and the resulted solutions were stirred for 5 min. Then, the Cu^{2+} ions preconcentrated onto the IIP nanoparticles were eluted using 5 mL of $0.1\,mol\,L^{-1}$ HNO_3, while stirring for 5 min. The results indicated that the recoveries of the copper were 99% and higher up to a sample volume of 300 mL. However, at higher sample volumes, the recovery decreased significantly. Thus, 300 mL was selected as the maximum sample volume in which the quantitative extraction of copper by the prepared IIP is possible.

3.3.3. *Equilibrium sorption time*

In a typical uptake kinetics test, 30 mg of the sorbent was added to 10 mL of a $1\,\mu g\,mL^{-1}$ solution of Cu^{2+} at pH 7.0. The resulting suspension was stirred for different periods of time (i.e., from 2 to 30 min) under magnetic stirring. After centrifugation, the supernatant solution was removed and the Cu^{2+} ions were determined by ICP AES. The results indicated that quantitative sorption (>99%) of Cu^{2+} can achieve over the entire time period range tested, indicating a very fast sorption kinetics of the Cu^{2+} on the imprinted polymeric nanoparticles. Such a fast sorption rate could be attributed to the formation of imprinted polymer materials in nano size scale during precipitation polymerization process, which results in increased surface area, more favorable accessibility of functional groups of the ligand in imprinted sites [53], high porosity of polymer network, related to consumption of more solvent during its synthesis, and the small size of the hydrated Cu^{2+} ion in relation to the average pore diameter of the prepared polymer, as supported by the results obtained from N_2 adsorption–desorption studies. Moreover, the presence of cross-linker ester groups can also facilitate the diffusion of water onto the hydrophobic polymeric network. In addition, the fast color change, from yellow to red, of polymer observed immediately after its addition to 10 mL of a $1\,\mu g\,mL^{-1}$ solution of Cu^{2+} at pH 7.0 is another support for fast kinetics of the sorption process.

3.3.4. *Adsorption properties*

Adsorption properties of polymer can be evaluated by adsorption isotherms in the batch experiments. These isotherms provide a relationship between the concentration of the analyte in solution and that adsorbed on the solid sorbent when the two phases are at equilibrium. Langmuir and Freundlich isotherms are usually used to analyze the sorption data in the IIP studies [13,15,24]; thus, in this work, we used these isotherms to study the adsorption properties of the IIP nanoparticles prepared for copper ions.

The Langmuir adsorption model is a theoretical equation and is applicable to homogeneous binding sites and assumes that the molecules are adsorbed at a fixed number of well-defined sites, each of which can only hold one molecule. These sites are also assumed to be energetically equivalent and distant to each other so that there are no interactions between molecules adsorbed on adjacent sites [54]. The Langmuir adsorption isotherm is expressed by Eq. (6).

$$Q = \frac{Q_{\max} b C_e}{1 + b C_e} \tag{6}$$

where Q is the amount of adsorbed Cu^{2+} ions on the IIP particles at equilibrium ($\mu mol\,g^{-1}$), C_e is the equilibrium concentration of Cu^{2+} ions in solution ($\mu g\,mL^{-1}$) and $Q_{\max}$ and b are Langmuir constants related to the maximum adsorption capacity and energy of adsorption, respectively. The Langmuir equation can be linearized

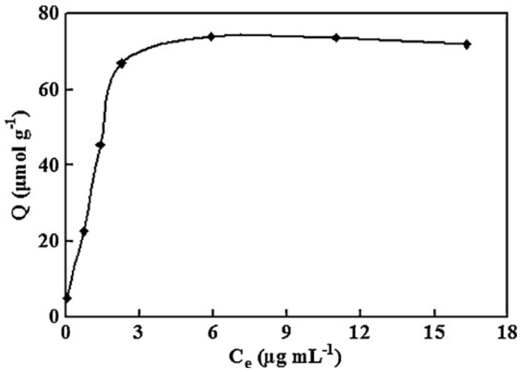

Fig. 8. Effect of Cu^{2+} equilibrium concentration on the adsorption capacity of Cu^{2+}–IIP (adsorption isotherm of Cu^{2+}–IIP): polymer weight 30 mg, sample volume 10 mL, pH 6.0, stirring time 30 min, temperature 25.0 °C.

in a normal form for the determination of Langmuir constants as:

$$\frac{C_e}{Q} = \left(\frac{1}{Q_{\max}}\right) C_e + \frac{1}{bQ_{\max}} \tag{7}$$

The Freundlich adsorption model is an empirical equation and is applicable to heterogeneous binding sites. The Freundlich isotherm is not restricted to the formation of a monolayer. The Freundlich adsorption isotherm is expressed by Eq. (8).

$$Q = K_F {C_e}^{1/n} \tag{8}$$

where K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Freundlich equation can be linearized in logarithmic form for the determination of Freundlich constants as:

$$\log Q = \left(\frac{1}{n}\right) \log C_e + \log K_F \tag{9}$$

The Freundlich isotherm does not predict saturation of the solid surface by the adsorbate and, thus, infinite surface coverage is predicted mathematically [15].

In several batch experiments, 30 mg portions of the imprinted sorbent were equilibrated with varying initial concentrations of Cu^{2+} (1–30 μg mL^{-1}) at pH 6.0. Although optimum pH was found as 7.0, the adsorption capacity of copper ions on the imprinted polymer was studied at pH 6.0, because the precipitation of Cu^{2+} ions at higher parts of the concentration range used does not occur at this pH. After 3 min, the equilibrium copper concentrations in solution and, consequently, the amount of the metal ion bound to polymer were determined by ICP AES.

The resulting plot of Q vs. C_e is shown in Fig. 8. As seen, the amount of Cu^{2+} ions adsorbed per unit mass of the imprinted nanoparticles increased linearly with the equilibrium concentration of copper(II) ions from 0.05 to 2.3 μg mL^{-1} and reached a plateau in the adsorption profile at 6 μg mL^{-1}. It should be mentioned that, because of precipitation of copper(II) at initial concentrations above 30 μg mL^{-1} at pH 6.0, higher copper(II) concentrations were not tested. As it is clear from Fig. 8, the maximum sorbent capacity is 73.8 μmol g^{-1}.

Based on Eq. (7), a plot of C_e/Q vs. C_e was found to be quite linear, revealing the fact that the adsorption obeys Langmuir adsorption model. The constants Q_{max} and b, determined from the Langmuir plot, were found to be 76.9 μmol g^{-1} and 1.2 mL μg^{-1}, respectively. Meanwhile, the plot of log Q vs. log C_e (Eq. (9)) was nonlinear, which obviously insisted that the adsorption does not obey the Freundlich adsorption model over the entire concentration range studied.

3.3.5. Selectivity study

Table 1
Distribution ratio (K_d), selectivity coefficient (k) and relative selectively coefficient (k') values of ion-imprinted polymer (IIP) and control non-imprinted polymeric (NIP) material for different metal ions.

Cation	K_d (IIP) (mL g^{-1})	K_d (NIP) (mL g^{-1})	k (IIP)	k (NIP)	k'[a]
Cu^{2+}	36746.8	1583.4	–	–	–
Ni^{2+}	344.5	276.9	106.7	5.7	18.7
Co^{2+}	256.8	214.3	143.1	7.4	19.4
Zn^{2+}	210.3	163.7	174.7	9.7	18.1
Mn^{2+}	143.2	111.1	256.7	14.2	18.0

[a] $k' = k(IIP)/k(NIP)$

Table 2
Performance characteristics of the preconcentration procedure.

Parameters	Cu
Precision (R.S.D.)	2.6%
Detection limit ($3S_b/m$)	0.10 ng mL^{-1}
Determination limits ($10S_b/m$)	0.33 ng mL^{-1}
Linear calibration range	1–100 ng mL^{-1}
Regression equation (after preconcentration)	Int. = 108701.4C_{Cu} + 593.9
Conventional regression equation	Int. = 1922.8C_{Cu} + 22.0
Enrichment factor	108701.4/1922.8 = 56.5

In ion-imprinted polymers, chelating sites possess a uniform distribution [22] and the cavities created after removal of template is complementary to the imprint ion in size and coordination geometries [29]. Moreover, the chelating ligands used in their preparation usually have selective affinities for the imprint ion. Thus, the IIPs are expected to possess good selectivities for the sorption of their imprint ions. It is worth mentioning that, in non-imprinted sorbents, the random distribution of ligand functionalities in polymeric network results in no specificity in the rebinding affinities.

In order to examine the selectivity of the imprinted nanomaterial, competitive sorption of Cu^{2+}/Ni^{2+}, Cu^{2+}/Co^{2+}, Cu^{2+}/Zn^{2+} and Cu^{2+}/Mn^{2+} from their binary mixtures was investigated in batch experiments. It should be noted that all of the selected competitor ions have the same charge and more or less similar ionic radius with Cu^{2+} ion. The initial concentrations of pair of metal ions (1 μg mL^{-1}) were extracted by 30 mg of imprinted material at pH 7.0. Table 1 summarizes the distribution ratios (K_d), selectivity coefficients (k) and relative selectively coefficients (k') calculated using Eqs. (3)–(5), respectively. A comparison of the selectivity results of the imprinted and control materials given in Table 1 clearly revealed the ion-imprinting effect of the prepared Cu^{2+} IIP nanoparticles based on 1-hydroxy-4-(prop-2′-enyloxy)-9,10-anthraquinone (AQ) as a vinylated chelating agent. The increased tendency of the IIPs for complex formation with Cu^{2+} ion, resulting from the imprinting process, is caused by the energy benefit due to formation of nondistorted complexes in comparison with non-imprinted samples [23]. The selectivity coefficients obtained on ion-imprinted polymeric nanoparticles revealed the fact that the quantitative removal and determination of Cu^{2+} ions can be achieved even in the presence of excesses of the interfering ions.

Table 3
Determination of copper in synthetic and real water samples.

Sample	Added (ng mL^{-1})	Found (ng mL^{-1})	Extraction (%)
Synthetic sample[a]	0	0	
	10	9.8	98.2 ± 2.3[b]
Tap water	0	10.8	
	10	20.4	96.6 ± 2.5
Well water	0	12.9	
	10	23.3	104.3 ± 2.6

[a] Solution contain Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} ions of 10 μg mL^{-1} concentrations.
[b] Standard deviation based on three replicate analyses.

Table 4
Sorbent characteristics of different copper(II) ion-imprinted polymers.

Ligand	Polymerization method	Detection system	Ads/des time (min)	Relative selectivity coefficient				Maximum sorbent capacity	LOD (ng mL^{-1})	Ref.
				k'_{Mn}	k'_{Co}	k'_{Ni}	k'_{Zn}			
VP/DBDA15C4[a]	Bulk	ICP AES	45/30	6.2	13.9	11.3	16.1	75.3 μmol g^{-1}	0.5	[4]
MAA/PAR[b]	Dispersion	FAAS	20/30	N.R.[c]	19.34	16.96	N.R.	37.4 μmol g^{-1}	0.1	[10]
MAH[d]	Dispersion	FAAS	60/120	N.R.	12.3	9.51	7.4	48 mg g^{-1}	0.4	[12]
CS[e]	Sol–gel	FAAS	30/30	N.R.	16.46	122.12	5.85	47.6 mg g^{-1}	0.83	[13]
MAA/diethylene triamine	Bulk	FAAS	30/N.R.	N.R.	N.R.	1.58	3.1	76 mg g^{-1}	0.5	[14]
L[f]	Bulk	ICP AES	30/N.R.	N.R.	64.38	208.3	49.7	29.8 mg g^{-1}	0.32	[20]
AQ	Precipitation	ICP AES	2/2	18.0	19.4	18.7	18.1	73.8 μmol g^{-1}	0.1	This work

[a] 2-Vinylpyridine/5,6;14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadecane-5,14-diene.
[b] Methacrylic acid/4-(2-pyridylazo)resorcinol.
[c] Not reported.
[d] Methacryloylamidohistidine.
[e] Chitosan-succinate.
[f] (2Z)-N,N'-bis(2-aminoethylic)but-2-enediamide.

3.4. Desorption studies

The influence of nature of mineral acid used as leachant on the desorption Cu^{2+} ions from the IIP nanoparticles was examined using 5 mL portions of 0.1 mol L^{-1} HNO_3, 0.1 mol L^{-1} HCl and 0.05 mol L^{-1} H_2SO_4, which resulted in respective percent desorptions of >99%, 98% and 97%. Thus, 0.1 mol L^{-1} HNO_3 was selected as leachant, not only because of its some better leaching characteristic over other two mineral acids but also because of its compatibility with ICP AES.

In order to study the optimum leachant concentration, several 5 mL portions of nitric acid solutions with different concentrations (i.e., 0.001, 0.01, 0.1 and 1.0 mol L^{-1}) were used for leaching of Cu^{2+} ions from the imprinted sites in the polymer matrix. It was found that desorption of Cu^{2+} ions increased with increasing nitric acid concentration (i.e., with respective percent desorptions of 90%, 96%, >99% and >99%). This is most possibly due to increased protonation of the hydroxylate sites of the printed polymer. Thus, 5 mL of 0.1 mol L^{-1} HNO_3 was selected as optimal leachant solution.

The influence of desorption time was also examined as follows. In several batch experiments, 30 mg of the sorbent was added to 10 mL of 1 μg mL^{-1} solution of Cu^{2+} at pH 7.0 for 3 min to complete sorption process. After centrifugation, the supernatant solution was removed and then 5 mL of 0.1 mol L^{-1} HNO_3 was added to sorbent containing Cu^{2+} ions. The resulting suspension was stirred for different time intervals (i.e., from 2 to 30 min) under magnetic stirring. After centrifugation, the supernatant acidic solution was removed and the Cu^{2+} ions were determined by ICP AES. The results indicated that quantitative desorption (>99%) of Cu^{2+} can achieve in all time intervals studied, revealing the fast kinetics of desorption process. Rapid color change of the polymeric nanoparticles containing Cu^{2+} ions immediately after addition of 0.1 mol L^{-1} HNO_3, from red to yellow, is a further support for the fast desorption of sorbent.

3.5. Repeated use

In order to examine the reusability of the prepared ion-imprinted polymer, the sorption experiments (sorption-desorption cycle) were repeatedly performed using the same nanoparticles. A 5 mL portion of 0.1 mol L^{-1} HNO_3 solution was used for elution of Cu^{2+} ions and regeneration of the nanoparticles. The sorption–desorption cycles were performed for six and twenty times. Each experiment was performed under the following optimal conditions: initial metal ion concentration, 1 μg mL^{-1}; amount of imprinted polymer, 30 mg; pH, 7.0; treatment period, 2 min. The results showed that Cu^{2+}-imprinted nanoparticles could be repeatedly used without any significant loss in the initial binding affinity. The relative standard deviations for six and twenty replicates with the same nanoparticles were found to be 1.7% and 2.1%, respectively.

3.6. Analytical performance

The analytical performance data for the batch preconcentration procedure are given in Table 2. The relative standard deviation for six separate batch experiments with 30 mg sorbent for the determination of 10 μg Cu^{2+} in 100 mL water was 2.6%. The limits of detection and quantitation, defined as $C_{LOD} = 3S_b/m$ and $C_{LOQ} = 10S_b/m$, where S_b is standard deviation of six replicate blank signals and m is slope of the calibration curve after preconcentration, for a sample volume of 300 mL, were found to be 0.10 and 0.33 ng mL^{-1}, respectively. The preconcentration procedure showed a linear curve within the concentration range from 1 to 100 ng mL^{-1}. The enrichment factor, defined as the ratio of the slopes of the linear sections of the calibration curves after (i.e., $\text{Int.} = 108701.4C_{Cu} + 593.9$, Table 2) and before (i.e., $\text{Int.} = 1922.8C_{Cu} + 22.0$, Table 2) preconcentration process, is calculated as $108701.4/1922.8 = 56.5$. Meanwhile, the preconcentration factor evaluated from the ratio of the sample volume (300 mL) to the leachant volume (5 mL), is 60.

3.7. Accuracy and analytical applications

The accuracy of the proposed method was evaluated by analyzing a certified reference material, NIST CRM 1643e (National Institute of Standard and Technology, Trace elements in water) with a copper concentration of 22.76 ± 0.31 ng mL^{-1}. The copper content obtained (mean ± S.D., $n = 3$) was 22.19 ± 0.54 ng mL^{-1}, which is in satisfactory agreement with the certified value.

Finally, the resulting Cu^{2+} ion-imprinted polymeric nanoparticles were applied to the determination of copper in synthetic, tap and well water samples. For the preconcentration of copper ions, 300 mL of the aqueous solution of real and spiked samples with Cu^{2+} ions was equilibrated with 30 mg of the Cu^{2+}-imprinted sorbent. The pH of solutions was adjusted at 7.0 and the resulted solutions were treated with IIP nanoparticles in stirred suspension for 2 min and then leaching processes were carried out by 5 mL of 0.1 mol L^{-1} HNO_3, while stirring for 2 min. The concentration of Cu^{2+} ions in leachant solutions were determined using calibration curve after analyzing by ICP AES, and the results are summarized in Table 3. The recoveries of Cu^{2+} ions from the real and spiked samples varied in the range of 95–105%. The results clearly indicate the suitability of AQ containing imprinted polymer for the perconcentration and determination of Cu^{2+} ions in different water samples.

4. Conclusions

The results obtained from this study clearly revealed that AQ can be used as a vinylated chelating agent in conjunction with ion imprinting technology to create binding sites with high affinities toward Cu^{2+} ions. The prepared ion-imprinted polymer nanoparticles possess an increased selectivity toward Cu^{2+} ion over a range of competing metal ions with the same charge and similar ionic radius. One of the most important characteristics of the prepared copper IIP is very fast sorption and desorption of Cu^{2+} ion, in a time period limit of 2 min. The adsorption isotherm of Cu^{2+} ion-imprinted polymer obeys the Langmuir adsorption model. The Cu^{2+}-imprinted nanoparticles can be repeatedly used and regenerated with no significant decrease in their binding affinities. The proposed Cu^{2+} IIP could be applied to the preconcentration and determination of copper content in real sample matrices. A comparison between the sorbent characteristics, including the nature of ligand, polymerization method, detection system, adsorption/desorption time, relative selectively coefficient, maximum sorbent capacity, limit of detection, of the proposed Cu^{2+}–IIP system with those of the previously reported ones (Table 4) clearly revealed that this sorbent can be categorized among the best copper IIPs ever reported, specially in minimum adsorption/desorption time.

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