

## Synthesis of Ion-Imprinted Polymer for Selective Separation of Copper(II) from Metal Ions Mixture

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Ion imprinted polymers (IIPs) draw great attention in various fields because of powerful selectivity to the target metal ions. Thus, the synthesis of copper-ion imprinted polymer (Cu-IIP) was performed by using copper ion and complexing agent rufigallol with ethylene glycol dimethacrylate (EGDMA) and 2,2-azobisisobutyronitrile (AIBN). Aqueous HCl was used to leach Cu<sup>2+</sup> ions from the imprinted polymer for creation of cavities of template, which is utilized for copper ions adsorption with high selectivity. The IIP were characterized using ICP-MS, FE-SEM and also solid state analysis by UV-visible NIR spectroscopy. FT-IR study confirmed the successful complexation of Cu-IIP. The optimum pH was found to be 6 and highest adsorption capacity was estimated about 112.5 mg g<sup>-1</sup>. Thus, IIP gave good selectivity to copper ions in presence of other transition metals and also IIP can be regenerated for eight times without a substantial loss in adsorption capacity.

**Keywords:** Ion imprinted polymer, Copper ion, Rufigallol, Selective separation.

### INTRODUCTION

Molecular imprinting technology allows us to synthesize the compounds with high specificity and selectivity receptor sites to the target molecule [1]. The molecular imprinted polymers (MIPs) are specific to identify the size, shape and functional group of template [2]. This technology has been applied in numerous fields of chemistry, pharmaceutical, biotechnology, biochemistry, *etc.* [3]. In many years back until now, molecular imprinting has become a well-known method used in the solid-phase extraction, catalysis, sensor design, as well as for protein separation, as receptor, antibody, enzyme mimics and also in one of the most important application which is in wastewater treatment [4].

Ion imprinted polymers (IIPs) are analogues to the molecular imprinted polymers (MIPs) since metal ions goes to the binding/adsorption event before imprinting process of the ion imprinted polymers while metal ions can be detected after cavity formation [5-8]. Ion imprinted polymers produces with the desired metal ions, which are placed in the specific sites of the imprinted polymers and moderate used as a selective absorbent of target metal ions [9]. The ion-imprinting is a specific complex

formation of the desired metal ion with ligand, which is capable of coordination process in the liquid phase before polymerization [10]. The ion imprinted polymers are effective in the solid-phase extractions [11], sensors [12] and membrane separations [13]. As reported, a amino-functionalized silica gel was used to prepare Fe(III)-imprinted polymers, which showed 25.21 mg g<sup>-1</sup> adsorption [14]. A Fe(III)-IIP was synthesized using methacrylamidoantipyrine and EGDMA and its adsorption capacity was found to 29.3 mg g<sup>-1</sup> [15].

Water polluted with heavy metals is a global danger that caused serious problems. All of these heavy metals like copper need to be detect and removed. The scientist developed several ethods such as bioremediation [16], physical adsorption and oxidation [17] to remove heavy metals from wastewater. Unfortunately, in this method only can remove various metals simultaneously but not specifically to the certain metal [18]. Because of this reasons, a new method known as ion imprinted polymers are attracting attention due to its capability to remove the desired metals effectively and selectively. Elemental copper and it's salts are important for catalysts and semiconductor industry [19-22]. Several report regarding the synthesis of ion imprinted polymers materials and their use in separation of

transition metal [23], copper [24] and actinide [25] metal ions. Rufigallol is a known compound and show an interesting behaviour in both materials and biological science.

In this study, we have used copper ions as a template element and rufigallol as a functional ligand. We have focussed on rebinding of copper ions to the template to find the selectivity of templates towards the metal. The Cu-IIP polymer was used successfully for extraction of target copper in real conditions.

## EXPERIMENTAL

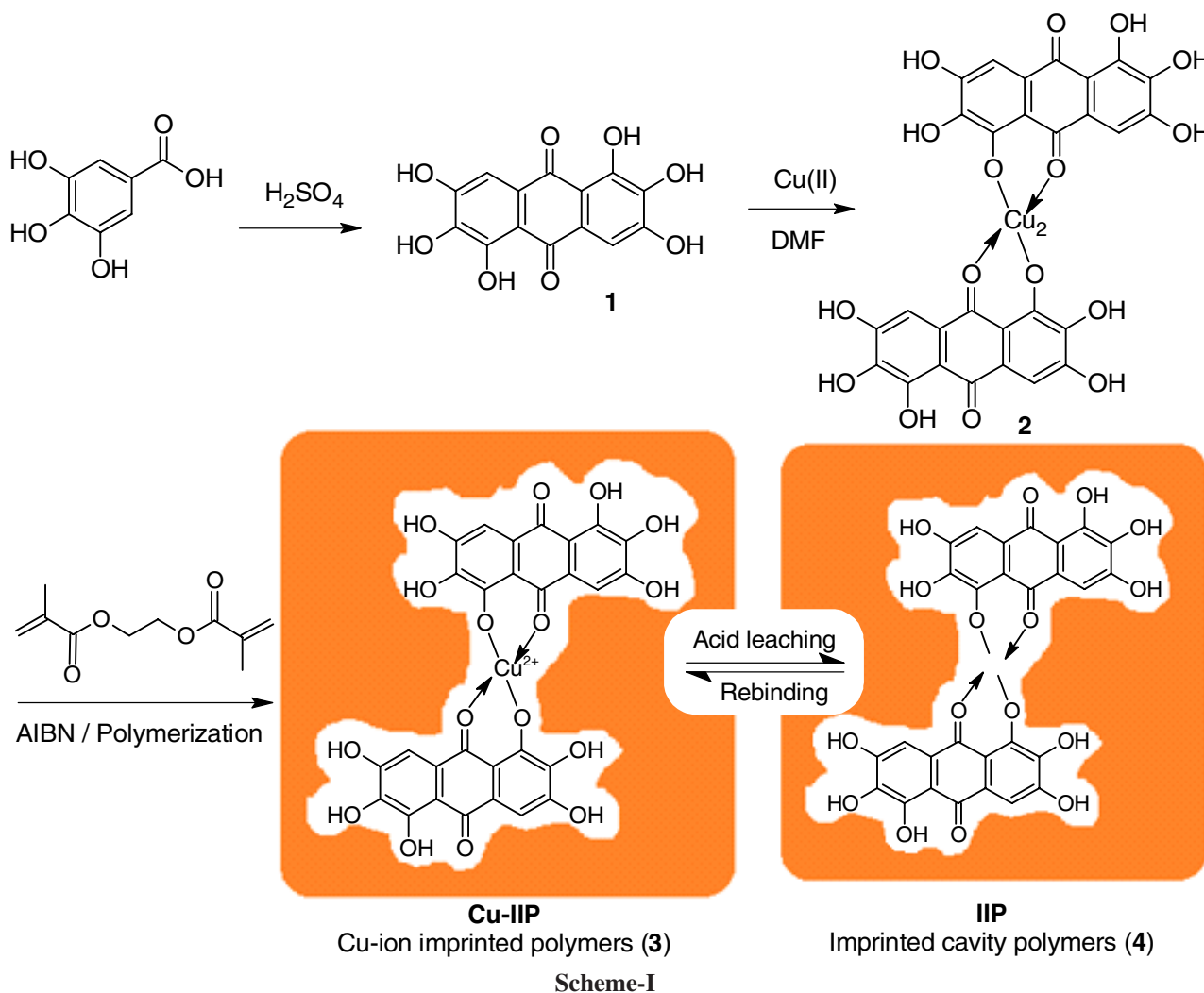
Gallic acid (Fluka), copper acetate (Fluka), acetic acid, sodium hydroxide (Aldrich), hydrochloric acid, dimethyl formamide (DMF), ethylene glycol-dimethylacrylate (EGDMA), 2,2-azobisisobutyronitrile (AIBN) (Aldrich) were used as received. Dimethyl formamide was refluxed over calcium hydride (Fluka) and distilled out before use.

The characterization of Cu-IIP was carried out by using several instruments. The structure of intermediate and ion imprinted polymers were determined by spectroscopic method. Perkin Elmer (670) FT-IR spectrometer was used to record the IR spectra. Bruker (DMX500) spectrometer was used to record both  $^1\text{H}$  NMR (500 MHz) and  $^{13}\text{C}$  NMR (125 MHz) spectra. FESEM was obtained with JEOL (JSM-7800F) to study the morphology of Cu-IIP. The solid state UV-visible NIR spectrophotometer (UV-2600 Shimadzu) was used to determine the

absorbance of complex and Cu-IIP. Metal ions concentrations were analysed by ICP-MS (Agilent 7500 series).

**Synthesis of rufigallol (1):** Gallic acid (10 g) was dissolved in concentrated  $\text{H}_2\text{SO}_4$  (40 mL) at  $100^\circ\text{C}$ . The reaction was stirred and the reaction flask was immersed into an oil bath. The temperature need to maintain at  $100^\circ\text{C}$ . After 3 h, the reaction mixture was cooled down to room temperature and crushed ice was added to the mixture. The reaction mixture was filtered and washed with distilled water to reduce the pH to 6. The solid compound was dried in the vacuum oven at  $70^\circ\text{C}$  for overnight to obtain compound **1** (Scheme-I).

**Synthesis of Cu-ion imprinted polymer (Cu-IIP) (3):** The imprinted polymer was prepared by thermal polymerization process. This reaction involved rufigallol as functional ligand, copper ion as a template, EGDMA as crosslinker and AIBN catalyst as free radical initiator. The rufigallol (152 mg) and  $\text{Cu}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$  (100 mg) that acts as template molecule were placed into 50 mL round-bottom flask and dissolved in DMF (20 mL) for at least 5 h to obtain a complex compound **2**. After the complex formation, covered the flask tightly and nitrogen gas was purged inside the mixture for about 15-20 min. While purging the gas, subsequently added EDGMA (500 mg) and AIBN catalyst (22 mg). The reaction mixture was leaved overnight in oil bath at  $60^\circ\text{C}$  to allow the polymerization process and the flask was fully sealed to prevent oxygen to enter the



flask and interrupt the process. The polymer that formed was stirred in methanol (300 mL) for about 10 min and the precipitate was settled down at the bottom of the beaker. The polymer was filtered and again washed with methanol for few times. The filtered polymer dried in the oven at 70 °C to a constant weight for compound **3** (Scheme-I).

**Extraction of Cu(II) from imprinted polymer:** In order to remove the template from polymer to obtain cavity polymer (**4**), molecular imprinted polymer need to be wash with the diluted acid. The prepared ion imprint polymer (100 mg) was washed with 2M HCl (20 mL). The reaction solution was stirred vigorously for 24 h. After the reaction was completed, compound was filtered and the solid was washed with methanol and dried in the oven at 70 °C to form cavity polymer IIP (Scheme-I). The filtrate was transferred into 50 mL volumetric flask for test using ICP-MS. The percentage of extracted Cu(II) was determined by eqn. 1, where  $C_i$  and  $C_f$  ( $\text{mg L}^{-1}$ ) are the concentrations of metal ions before and after extraction.

$$\text{Extraction (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

The sorption capacity,  $Q$  ( $\text{mg g}^{-1}$ ) of IIP relative to imprinted metal ions was calculated by eqn 2, where  $V$  is the volume of the solution,  $m$  is the mass of IIP material (mg).

$$Q = \frac{C_i - C_f}{m} \times V \quad (2)$$

The distribution ratio,  $K_d$  ( $\text{mL g}^{-1}$ ) of metal ions between IIP and aqueous solution was also calculated by eqn. 3, where  $V$  is the volume of initial solution and  $m$  is mass of IIP material (mg).

$$K_d = \left( \frac{C_i - C_f}{C_f} \right) \frac{V}{m} \quad (3)$$

Selectivity coefficients ( $k$ ) for  $\text{Cu}^{2+}$  and ion relative to foreign ions in the solution are defined as:

$$k_{\text{Cu}^{2+}/\text{M}^{n+}} = \frac{K_d^{\text{Cu}^{2+}}}{K_d^{\text{M}^{n+}}} \quad (4)$$

where  $K_d^{\text{Cu}^{2+}}$  and  $K_d^{\text{M}^{n+}}$  are the distribution ratios of copper and foreign metal ions, respectively.

## RESULTS AND DISCUSSION

Rufigallol (**1**) was synthesized from condensation of gallic acid under sulfuric acid treatment. Then copper-complex (**2**) was produced by compound **1** with DMF as porogen solvent at room temperature. The dark-brown complex was formed as copper IIP nanoparticles, which is converted into Cu-IIP using free radical polymerization method. In polymerization procedure, solution complex of **2** with a cross-linker agent EGDMA was stirred at 60 °C for 48 h in presence of a free radical initiator (AIBN). The polymer was precipitated in methanol and dried Cu-IIP at 50 °C to yield complex **3**. The imprinted ion (*i.e.*  $\text{Cu}^{2+}$  ion) was leached for cavity created in Cu-IIP by 2 M HCl solution. Thus, copper was adsorbed further for repeated adsorption by IIP **4** (Scheme-I).

**FT-IR analysis:** FT-IR spectra of Cu-IIP and other compounds were determined using KBr pellet and spectra are shown

in Fig. 1. The rufigallol (**1**) shows two peaks at  $3280 \text{ cm}^{-1}$  for OH groups and  $1640 \text{ cm}^{-1}$  for ketone functional groups (Fig. 1a). In case of Cu-IIPs (**2**) (Fig. 1b), only one broad absorption band was present at  $3480 \text{ cm}^{-1}$  assigned to O-H stretching band, which is shifted from  $3280 \text{ cm}^{-1}$  for coordination bonding and  $1640 \text{ cm}^{-1}$  is also shifted to  $1660 \text{ cm}^{-1}$  due to coordination with metals ions ( $\text{Cu}^{2+}$ ). Additional stretching bands for aromatic are retains for Cu-IIP. A cross-linking agent EGDMA having ester functional group, which was appeared at  $1728 \text{ cm}^{-1}$  for Cu-IIP, which confirmed the formation of polymer complex as shown in Fig. 1b. Generally, IR spectra can be used for proof of functional groups in the materials.

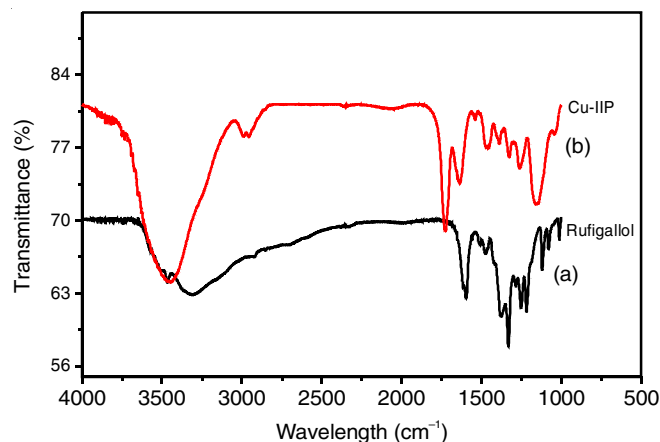


Fig. 1. IR spectra of rufigallol (a), polymer bind with  $\text{Cu}^{2+}$  ions (b)

**FE-SEM analysis:** Scanning electron microscopy was performed to find the difference on the surface properties for the functional monomer and polymers. It shows very clearly the morphological difference between the functional monomer which is rufigallol and polymer. The synthesized compounds including Cu-IIP were evaluated by scanning field emission electron microscopy (FE-SEM) to investigate the surface morphological properties. The FE-SEM images of synthesized polymers were presented in Fig. 2a and b. The micrograph under the magnifications 20,000 clearly showed the rough surface of rufigallol (**1**) (Fig. 2a) having three-dimensional wood like shape with different sizes and a small number of agglomerations were found on the surface of Cu-IIP (**3**) (Fig. 2b). The surface morphology of Cu-IIP also rough with variable spherical shape due to the compound is polymeric nature in structurally. Overall, Cu-IIP (**3**) possesses distinct morphology compared to organic ligand of rufigallol.

**UV-visible absorption:** Cu-IIP (**3**) showed stable physical and chemical properties of copper ions as shown in Fig. 3. The reflectance spectra of Cu-IIP (**3**) was observed to dissimilar from non-imprinted rufigallol (**1**). Thus, a broad peak at approximately 700 nm was observed for Cu-IIP (Fig. 3b), whereas rufigallol did not exhibits any peak around 600 to 900 nm, because no complex formation with compound **1** (Fig. 3a). The reflectance spectra of Cu-IIP showed the new peak at approximately 700 nm due to coppers ions, which proof the charge transfer ( $\pi$ - $\pi$  transition) complex was observed which strong evidence for the coordination-bonding occurred in the complex.

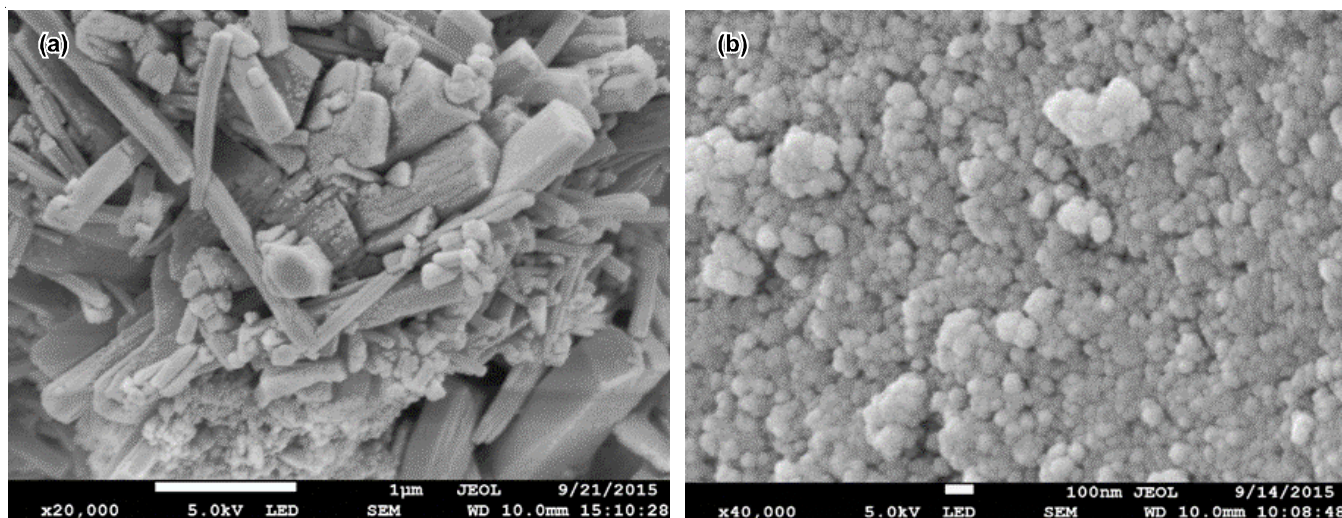


Fig. 2. SEM images rufigallol (a) and copper ions imprinted polymer with rufigallol (b)

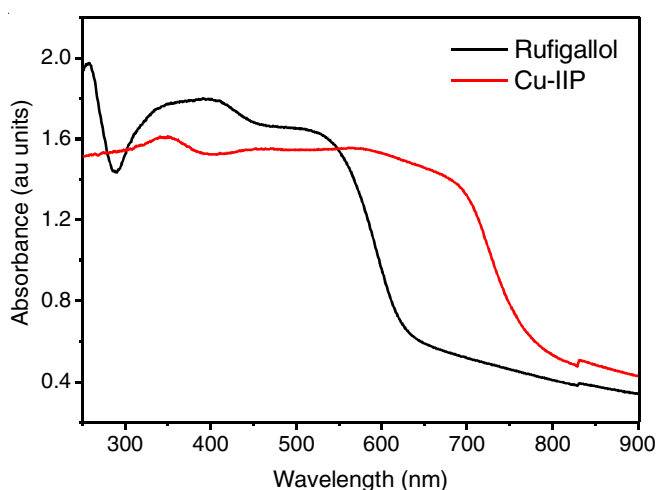


Fig. 3. UV-visible absorption spectra for complexation of Cu-IIP and rufigallol

### Sorption/desorption studies

**Effect of pH:** After extraction, proper eluent and retained copper ions,  $\text{Cu}^{2+}$  ions was removed from Cu-IIP (3) with 2 M HCl as aqueous solutions to produced IIP (4). Thus, bounded copper ions was fully desorbed by 20 mL of 2M HCl solution to obtained the recovery of 99 % for copper ion as estimated from eqn. 1 as shown in Fig. 4. This solution may exhibits polar character, which electrostatically disorder the binding interaction between copper ions and IIPs [21]. The coordination spheres of copper ions is disordered and copper ions were liberated from  $\text{Cu}^{2+}$  templates into the desorption agent as aqueous HCl solution. Literature survey revealed that binding properties of metal ions are greatly pH dependent [21-23]. The concentration of soluble metal species are actively influences the precipitation of metal ions in the absence of complexing agents. The more general batch adsorption procedure was used to find the effect of pH on the uptake of copper ions.

Exactly 20 mL solutions containing  $50 \text{ mg L}^{-1}$  of copper ions at various pH (2-9) were considered according the reported procedure [21]. Fig. 4 shows the effect of pH on the extraction (%) of  $\text{Cu}^{2+}$  ions. It was observed from Fig. 4, the adsorption of  $\text{Cu}^{2+}$  ions increases with the increasing of pH at 6. At the

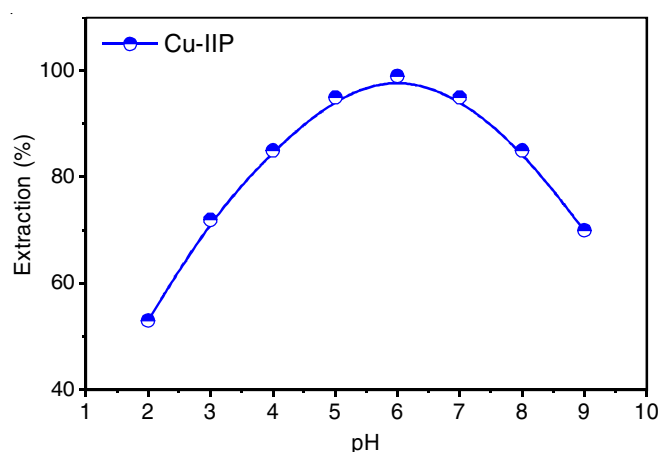


Fig. 4. Effect of pH on the extraction of copper ions by IIP (4)

higher pH beyond 7, precipitation of copper ions was occurred, whereas the protonation of binding sites of Cu-IIP was increases at lower pH decreases adsorption value. Consequently, either  $\text{Cu}^{2+}$  with rufigallol complex is not stable at low pH or the aggressive adsorption of proton and  $\text{Cu}^{2+}$  ions by the ligands at lower pH values is reduced the performance of extraction [24].

**Adsorption capacity:** Obviously ion imprinted polymers exhibit absorptive property as compare with other absorbent and extraction capacity usually expressed as maximum metal ions adsorbed per gram of IIPs. The optimum pH 6 was chosen to find the adsorption properties at various concentration of copper ions in solutions. The adsorption capacity ( $Q$ ) is expressed as the amount of metal ions adsorbed per gram of the sorbent and  $Q$  is the important parameter to determine the efficiency of IIPs [25]. The more general batch adsorption method was used for find the maximum adsorption values of  $\text{Cu}^{2+}$  on IIP. Thus, 40 mg of IIP (4) was equilibrated with 20 mL of copper solutions with various concentrations ( $10\text{-}50 \text{ mg L}^{-1}$ ) at optimum pH 6. Generally, precipitation of  $\text{Cu}^{2+}$  ions at pH 6 does not occurred with this limit of copper concentration. The adsorption behaviour of ion imprinted polymer with this parameters are given in Fig.5.

The maximum adsorption capacity ( $Q$ ) of ion imprinted polymer was calculated to be  $112.5 \text{ mg g}^{-1}$  at pH 6 by using

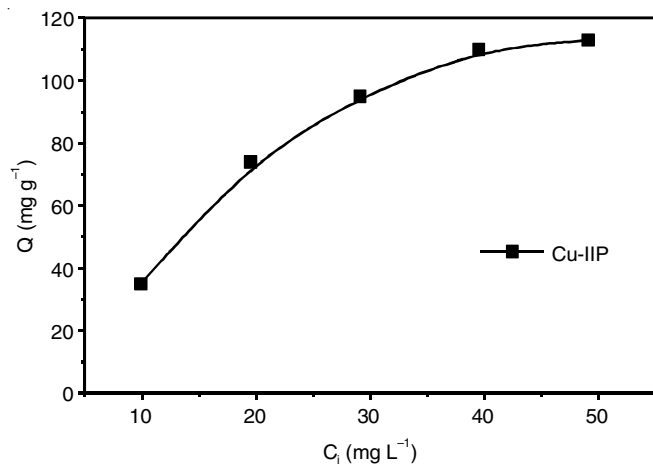


Fig. 5. Effect of concentration solution on the adsorption of copper ions by IIP (4)

eqn. 2, which was presented in the extraction efficiency. The  $\text{Cu}^{2+}$  ions adsorbed per unit mass of ion imprinted polymer was increased linearly at a constant amount of ion imprinted polymer particles. The adsorption decreased similar fashion with the initial concentration of  $\text{Cu}^{2+}$  ions, which represents unsaturation of the active cavities on the ion imprinted polymer by copper ions. Thus, imprinting procedure plays an important role in the absorption behaviour of Cu-IIP polymer.

**Selectivity:** To find the selectivity of IIP (4) towards metal ions, a series of batch adsorption experiments is performed with IIP (4) and pairs of  $\text{Cu}^{2+}$  and coexisting cations (some transition metals cations) were extracted by 40 mg of Cu-IIP at pH 6. On the other hand, IIP and pairs of  $\text{Cu}^{2+}$  with selected cations are also used for extraction using same amount (40 mg) of ion imprinted polymer at pH 6. Simultaneously adsorption property of copper ions with some cations for ion imprinted polymer particles in their mixture was evaluated under optimum conditions. Thus, distribution ratios ( $K_d$ ) and selectivity coefficients ( $k$ ) for  $\text{Cu}^{2+}$  ions relative to foreign cations were estimated by eqns 3 and 4, respectively. The results for  $K_d$  and  $k$  are presented in Table-1.

Cation	$K_d$ (mL g <sup>-1</sup> )	$k$
$\text{Cu}^{2+}$	352.5	–
$\text{Fe}^{3+}$	10.2	11.3
$\text{Cr}^{3+}$	8.5	7.7
$\text{Ni}^{2+}$	8.2	7.2
$\text{Co}^{3+}$	7.6	6.8

The competitive adsorption property of ion imprinted polymer for  $\text{Cu}^{2+}$  ion is higher than Cu-IIP-polymer beads due to the nature of ligand atoms accepted electron form copper ion. However, ion imprinted polymer shows for the competitive adsorption capacity. Table-1 can be used to compare the selectivity results, which clearly given the scenario of ion-imprinted effect. In this study, imprinted polymer was produced with copper metal ions complex as template, so three-dimensional cavities is formed by copper leaching with HCl and imprinted polymers are more selective for corresponding coppers ions with rifigallol

ligand. In principle, the cavities produces with a specific shape and size of template of imprinted polymer allows to accommodate by the corresponding metals ions.

The proposed ion-imprinted polymer showed the high selectivity to copper ions and a substantial difference of the binding capacity of  $\text{Cu}^{2+}$  ions and competitor metal ions. It was observed that prepared Cu-IIP can be utilized as a selective adsorbent for extraction of copper ions in the presence of other transition metal cations in various real and synthetic medium.

**Regeneration and reusability:** The prepared ion-imprinted polymer reusability test used in adsorption-desorption system without significant changing in the absorption capacity is an important feature due to an economic point of view. To determine the reusability test, 40 mg of IIP (4) was used in adsorption-desorption cycle for eight times under optimum condition. The results show that Cu-IIP can be reused in eight adsorptions-desorptions cycles without significant change was observed in the absorption capacity. Therefore, absorption capacity is decreased about 8 % after 10 times using the proposed Cu-IIP.

## Conclusion

In this work, copper ion-imprinted polymer was synthesized using copper ions and selected complexing ligand rufigallol in the presence of EGDMA as cross-linker and AIBN as initiator. The template of copper ions was removed by leaching the IIP with HCl solution for recognition and separation of copper ions from the mixture of other transition metal ions. The maximum adsorption value was observed as 122.57 mg/g at optimum pH 6. This Cu-IIP exhibits strong selectivity to copper ions in the presence of coexisting cations. The study showed that the ion-imprinted polymer can be repeatedly use and regenerated for eight times without any substantial loss in its original strength of extraction and performances.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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