Preparation of a New Cd(II)-Imprinted Polymer and Its Application to Preconcentration and Determination of Cd(II) Ion from Aqueous Solution by SPE-FAAS

Teguh Wirawan[1], Ganden Supriyanto[2,3,*], and Agoes Soegianto[4]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Mulawarman University, Samarinda 75119, East Kalimantan, Indonesia

[2]Department of Chemistry, Faculty of Science and Technology, Airlangga University, Surabaya 60115, East Java, Indonesia

[3]Laboratory of Sensor and Biosensor, Institute of Tropical Diseases, Airlangga University, Surabaya 60115, East Java, Indonesia

[4]Study Program of Environmental Science and Technology, Department of Biology, Faculty of Science and Technology, Airlangga University, Surabaya 60115, East Java, Indonesia

** **Corresponding author:***

tel: +62-8155203377

email: ganden-s@fst.unair.ac.id

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Abstract: *A novel ion Imprinted polymer (IIP) material with 8-hydroxyquinoline (8HQ) (the complexing ligands), methacrylic acid (MAA) (the monomers), ethylene glycol dimethacrylate (EGDMA) (the crosslinker agent), benzoyl peroxide (the initiator), and ethanol-acetonitrile (2:1) (the porogen) as adsorbent for the determination of cadmium by solid phase extraction–flame atomic absorption spectrometry (SPE-FAAS) has been synthesized. Synthesis of IIP was done by precipitation polymerization method. The imprinted Cd(II) ions were removed by leaching method using 1 mol L^{-1} nitric acid. The IIP was characterized by Fourier transform infra-red (FT-IR) spectroscopy and scanning electron microscopy (SEM) to ensure successful synthesis of IIP. The experimental parameters for SPE extraction, such as pH of the sample, loading rate, and elution rate, have been optimized. The optimum pH for quantitative Cd(II) retention was 6, and the elution was completed with 2 mL of 1.0 mol L^{-1} nitric acid. The optimum loading rate was 0.5 mL min^{-1}. Under optimum conditions, the proposed method with theoretical enrichment factor 50 times has a detection limit of 0.5 μg L^{-1} and the recovery of 97.75%.*

Keywords: *cadmium(II); solid phase extraction; ion imprinted polymer; preconcentration*

■ INTRODUCTION

Heavy metals are considered to be toxic to the environment. One of the toxic heavy metals is cadmium which is released into the environment by industrial wastewater. The most common industries releasing cadmium in their effluents are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining, and refining process [1-2].

Cadmium is a naturally occurring metal and known as an extremely toxic. Cadmium causes nausea, salivation, muscular cramps, chronic pulmonary problems, skeletal deformity, hypertension, proteinuria, kidney stone formation, osteoporosis, non-hypertrophic emphysema, anemia, eosinophilia, anosmia, chronic rhinitis, and Itai Itai disease. A high percent of accumulated cadmium is accumulated in the kidney and liver. Cadmium(II) ions may replace zinc(II) ions in some enzymes thereby affecting the enzyme activity in biological systems. Cadmium is also classified as a category 1 carcinogen (the human carcinogen) by the International Agency for Research on Cancer (IARC) [3-6].

The presence of cadmium in the waters is generally in a very low concentration, so an adequate analytical method is required. Several analytical techniques including cation exchange resin method [7], the competitive chelation method [8], stripping voltammetry [9], dialysis [10], ion-selective electrodes [11], and permeation liquid membrane [12] have been used for the determination of cadmium in different matrixes. Most of these methods suffer from chemical interferences, competition effects, disturbance of solution equilibrium, long equilibrium time, poor on limits of detection, poor preconcentration, and poor selectivity [13-15]. Preconcentration techniques have been developed to improve sensitivity. One of them is the solid phase extraction (SPE).

Solid-phase extraction (SPE), also known as solid-liquid extraction is a separation technique that is used to separate the analyte from a mixture, using their physical and chemical properties. The basic principle of SPE can be described as the transfer of analytes from the liquid phase into the solid phase. The analyte after sorption on the solid phase is desorbed with a suitable solvent. The solid phase extraction method is an alternative to replace solvent extraction. Solid phase extraction is a chromatographic sample preparation technique that is used for the separation, purification, and preconcentration of chemical compounds from solution [16-17]. In SPE, the sample is detained or absorbed and later eluted adsorbent with elution in one stage or gradient. There are several advantages when compared with solvent extraction, including low cost, reducing the use of hazardous solvents, decreasing time consumption, absence of emulsion [18-19], easy to storage and transport [20], the desired component can be taken by using a selective solvent [21], and can be used for the separation and purification [22]. One of the new sorbents is an ionic-imprinted polymer (IIP). The ion-imprinting idea is based on the formation of a complex from the metal ion with a ligand and its subsequent immobilization in a cross-linked polymeric matrix. Upon metal ion extraction from the polymeric body spatially pre-arranged binding sites are left in the sorbent structure [23]. The selectivity of IIP is caused by the following factors such as the specificity of interaction of a ligand with the metal ion, the coordination geometry and the coordination number of metal ion, the charge of the metal ion, and the size of the metal ion [19].

Recently, IIP has been growing rapidly as an adsorbent for SPE because it has the advantage on the enrichment factor and high selectivity. Applications of IIP as adsorbent in the SPE has been widely reported to the extraction of arsenic [24], iron [25-26], cadmium [23,27-28], mercury [29], copper [30], lead [31-33], and zinc [34-35].

In this paper, we report the development methods of cadmium preconcentration in SPE. Cadmium concentration was analyzed using flame atomic absorption spectrophotometer (FAAS). The IIP was synthesized using 8-hydroxyquinoline (8HQ) as complexing ligands, methacrylic acid (MAA) as the functional monomer and ethylene glycol dimethacrylate (EGDMA) as agents of cross-linking. Characterization of the IIP was investigated using Fourier transform infrared spectrophotometry (FTIR) and scanning electron microscopy (SEM). The experiment parameter such as pH of the solution, flow rate, volume of HNO_3 for elution was investigated. This method was applied for the enrichment of trace amount of cadmium ion from aqueous solutions.

■ EXPERIMENTAL SECTION

Materials

The materials used were $Cd(NO_3)_2{\cdot}4H_2O$ (Merck, Germany), HNO_3 (Merck, Germany), 8-hydroxyquinoline (8HQ) (Sigma Aldrich, US), methacrylic acid (MAA) (Sigma Aldrich, US), ethylene glycol dimethacrylate (EGDMA) (Sigma Aldrich, US), benzoyl peroxide (Merck, Germany), ethanol (Merck, Germany), and acetonitrile (Merck, Germany).

Instrumentation

The characteristic of functional groups among adsorbent was confirmed by Fourier transform infrared spectroscopy (Perkin Elmer). The surface morphological image of adsorbent was obtained by scanning electron microscopy (FEL, Inspect-S50). The concentration of cadmium was analyzed by flame atomic absorption spectrophotometer Hitachi type Z-2000. A pH-meter (Mettler Toledo) was used for the pH adjustments.

Procedure

Preparation of IIP

The ionic imprinted polymer was synthesized following the method proposed by Barciela-Alonso et al. [36]. In the glass tube, 0.0309 g (0.1 mmol) $Cd(NO_3)_2 \cdot 4H_2O$ and 0.0363 g (0.25 mmol) 8-hydroxyquinoline was mixed in 60 mL of porogen (2:1 ethanol-acetonitrile). This solution was stirred for 30 min with a magnetic stirrer. Then, 0.34 mL (4 mmol) of methacrylic acid (monomer), 0.0485 g (0.2 mmol) of benzoyl peroxide (initiator), and 3.77 mL (20 mmol) of ethylene glycol dimethacrylate (cross-linker) were added, the glass tube purged with nitrogen for 5 min and immediately sealed. Precipitation polymerization was carried out by heating in a water bath at 60 °C for 8 h while stirring with a magnetic stirrer. The polymer obtained was filtered, washed with ethanol, and oven-dried for 2 h at 60 °C. The cadmium ions were leached from the polymer by using 100 mL of 1 mol L^{-1} HNO_3 in magnetic stirrer for 30 min. The IIP was washed with distilled water, filtered, and dried at 100 °C for 24 h. The same procedure, except the presence of $Cd(NO_3)_2 \cdot 4H_2O$, and leaching, was applied for preparing non-imprinted polymer (NIP). The polymer was synthesized by the same procedure, except the presence of 8HQ, $Cd(NO_3)_2 \cdot 4H_2O$ and leaching. The 8HQ, MAA, EGDMA, polymer, and IIP were characterized by FTIR. The IIP and NIP were characterized by SEM.

Effect of pH

The effect of solution pH was tested by shaking 0.01 g IIP and 20 mL of the Cd(II) solution at various pH for 10 min. The pH of the sample solutions was varied from pH 4 to 8. The IIP was separated by filtration, and the concentration of Cd(II) in the filtrate was determined by FAAS.

Effect of eluent volume

A cartridge with an i.d. of 5 mm was filled with 0.1 g of dry IIP. 50 mL of 2.5 mg L^{-1} Cd(II) solution, adjusted to pH 6, was then passed through the column. Then the solution of 1 mol L^{-1} HNO_3 was passed to desorb Cd(II) from the cartridge. The volume of HNO_3 was varied from 0.5 to 5.0 mL. The eluate that contains Cd(II) was determined by FAAS.

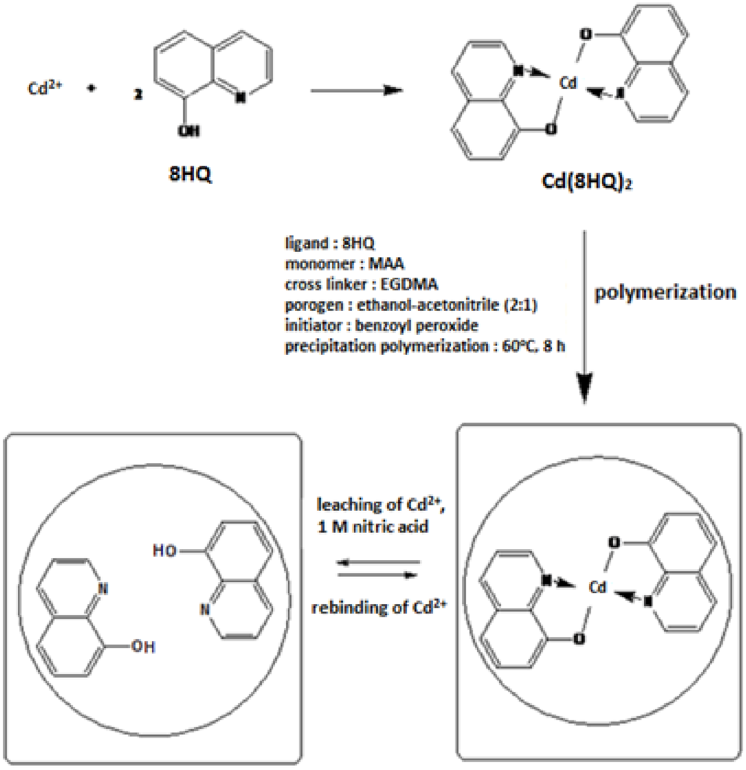

Fig 1. Illustration of IIP formation

Effect of flow rate

A cartridge with an i.d. of 5 mm was filled with 0.1 g of IIP. 50 mL of 2.5 mg L^{-1} Cd(II) solution, adjusted to pH 6, was passed through the column at various of flow rate. The flow rate was varied from 0.18 to 2.17 mL min^{-1}. Then, Cd(II) was eluted from the column with 2 mL of 1 mol L^{-1} HNO_3, and concentration of Cd(II) was then determined by FAAS.

Solid phase extraction

A cartridge with an i.d. of 5 mm was filled with 0.1 g of IIP. The sorbent was conditioned by passing 3 mL of buffer pH 6. For the loading of the analyte, the pH of Cd(II) standard solution was adjusted to pH 6 and passed through the column at a flow rate of 0.5 mL min^{-1}. Then, Cd(II) was eluted from the cartridge with 2 mL of 1 mol L^{-1} HNO_3, and concentration of Cd(II) was determined by FAAS.

■ RESULTS AND DISCUSSION

The new material was prepared by using 8-hydroxyquinoline (8HQ) as complexing ligands, methacrylic acid (MAA) as the monomer and ethylene glycol dimethacrylate (EGDMA) as agents of cross-linking. The polymer was synthesized by precipitation polymerization technique. The synthesis of IIP was carried out in three step (Fig. 1), i.e., (1) The complexation Cd(II) with 8HQ (2) the copolymerization of monomer (MAA) in the presence of the template (Cd(II)), and (3) the removal of the template after copolymerization from the polymer.

Characterization of IIP

The FTIR spectra of complexing ligand (8HQ), monomer (MAA), crosslinker (EGDMA), polymer, and IIP are presented in Fig. 2. The intense absorption centered at 1724 cm^{-1} in spectra polymer (Fig. 2(b)) was assigned to carbonyl groups from EGDMA and MAA. The polymer formed by the addition reaction of the C=C double bond to a single C-C bond. It is shown in the FTIR spectra of polymer that is absent a peak at 1524 cm^{-1} when compared to spectra of MAA (Fig. 2(d)). This confirmed the successful polymerization of the MAA and EGDMA. The intense absorption centered at 1492 cm^{-1} in spectra IIP (Fig. 2(a)) was assigned to C=C aromatic groups from 8HQ (Fig. 2(e)). The presence of a C=C aromatic group on the spectra FTIR of IIP when compared with the FTIR spectra of polymer, it shows the successful synthesis of IIP.

Scanning electron microscopy (SEM) images were presented in Fig. 3. The textural characteristics were closely examined at 10,000× magnification. The particles of both NIP and IIP were present in a spherical shape. The SEM images of IIP (Fig. 3(b)) physically look more cavities than NIP (Fig. 3(a)).

Influence of Initial pH on Cd(II) Adsorption

The influence of the initial pH on adsorption of Cd(II) on the IIP was studied to determine the optimum pH. The pH of the solution has been found to be the most

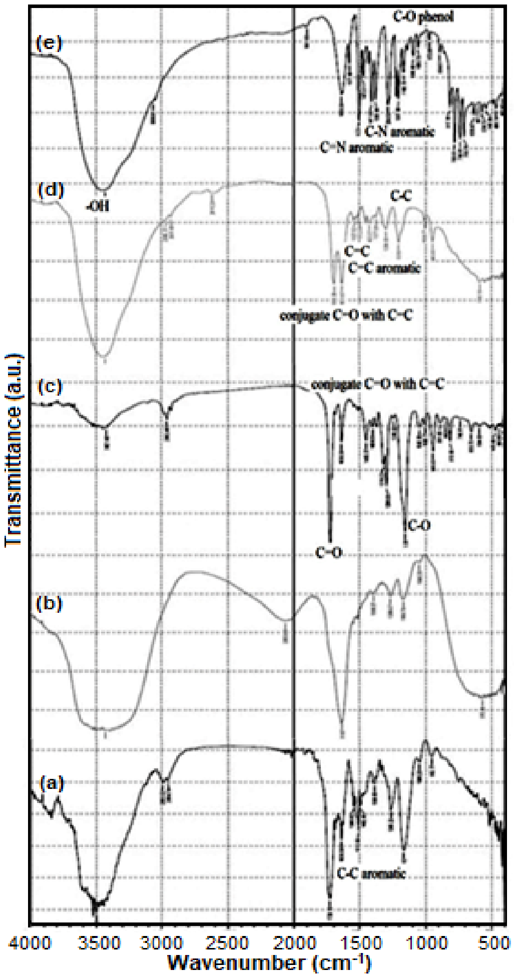

Fig 2. FTIR spectra of (a) IIP, (b) polymer, (c) EGDMA, (d) MAA, and (e) 8HQ

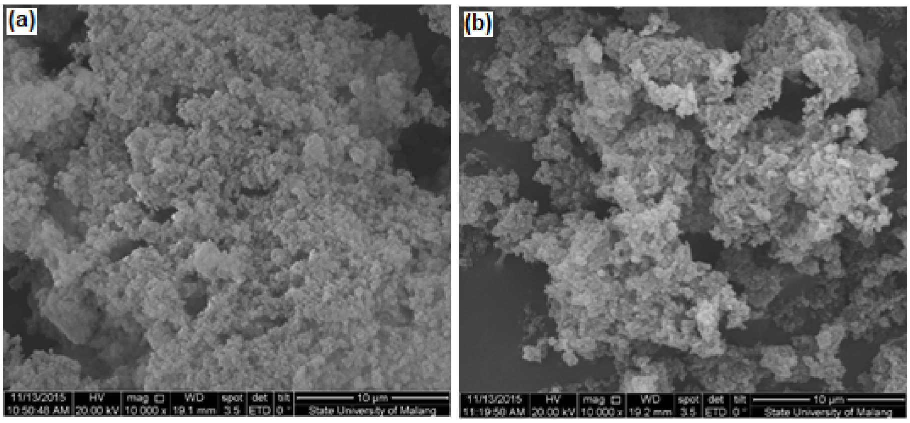

Fig 3. SEM images of (a) NIP and (b) IIP

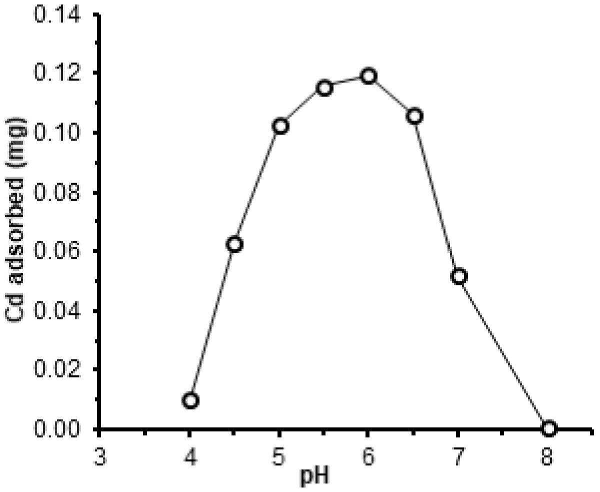

Fig 4. Influence of pH on the adsorption of Cd(II) on IIP

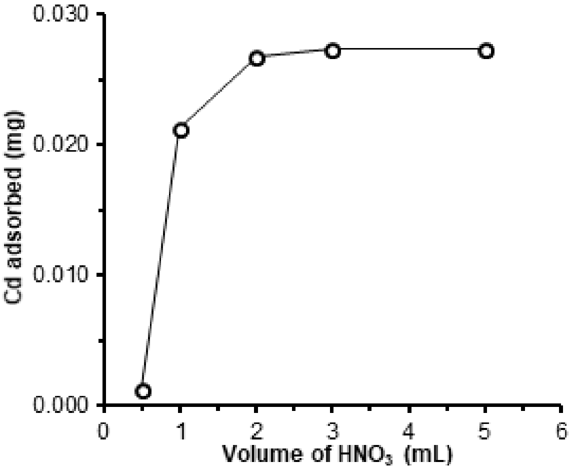

Fig 5. Influence of eluent volume on the eluted Cd(II) from IIP

important for adsorption heavy metals onto the adsorbent. It influences the speciation of metal ions and the ionization of functional groups on the adsorbent surface active sites [37-38].

The adsorption of Cd(II) as a function of the pH is shown in Fig. 4. The adsorption of Cd(II) increased greatly between pH 4 to 5.5 and then almost constant from 5.5 to 6, and then gradually decreased. At low pH, there are many H^+ in the solution, and the higher concentration of H^+ competes with Cd^{2+} for binding to the negatively charged active sites on the adsorbent actives sites [39]. The optimum of pH for adsorption Cd(II) on IIP is at pH 6. At pH above 7, adsorption decreases because there are a large amount of OH^- ligands in the solution [40]. At a pH of above 7, only $Cd(OH)^+$ and $Cd(OH)_2$ significantly contribute to the total cadmium in a solution as shown in the following possible reactions [41]:

$$Cd^{2+}(aq) + OH^-(aq) \rightarrow Cd(OH)^+(aq)$$

$$Cd(OH)^+(aq) + OH^-(aq) \rightarrow Cd(OH)_2(s)$$

Influence of Eluent Volume

The influence of the eluent volume on adsorption of Cd(II) on the IIP was studied. The HNO_3 was used as an eluent. It was used to dissociate the bond between the analyte and the adsorbent. After sample loading, the adsorbed Cd(II) was eluted by passing 1 mol L^{-1} HNO_3 at different volume (from 0.5 to 5 mL), and the result was presented in Fig. 5. The recovery of Cd(II) was increased greatly from 0.5 to 1 mL and then increased slightly from 1 to 2 mL. The volume above 2 mL had a constant recovery of Cd(II), and volume 2 mL was then chosen as an optimum volume.This result was similar to the study by Ebrahimzadeh et al. [42] which obtained that increase in volume and concentration of eluent caused higher recovery.

Influence of Flow Rate

The flow rate of the sample is related to the time of interaction between the analyte and the adsorbent. The higher flow rate will be more advantageous regarding obtaining a high enrichment factor because the higher sample volume is loaded into the column. But this is limited by the adsorption kinetics [23]. The sample flow rate through the sorbent should be low enough to enable efficient retention of the analytes, and high enough to avoid excessive duration analysis [16]. Different experiments were performed to find the optimum flow rates for the Cd(II) standard solution loading. The solution of Cd(II) standard was passed at a different flow rate (from 0.18 to 2.17 mL min^{-1}). As shown in Fig. 6, concentration of Cd(II) decrease for flow rates larger than 0.5 mL min^{-1}. The flow rate of 0.5 mL min^{-1} was chosen as the optimum flow rate to decrease the time needed for analysis.

Analytical Characterization

The limit of detection (LoD) and limit of quantification (LoQ) were calculated according to LoD = (3SD)/m and LoQ = (10SD)/m, where SD is the standard deviation and m is the slope of the calibration graph. The calibration graph of Cd(II) without preconcentration and with 50-fold theoretical preconcentration was presented

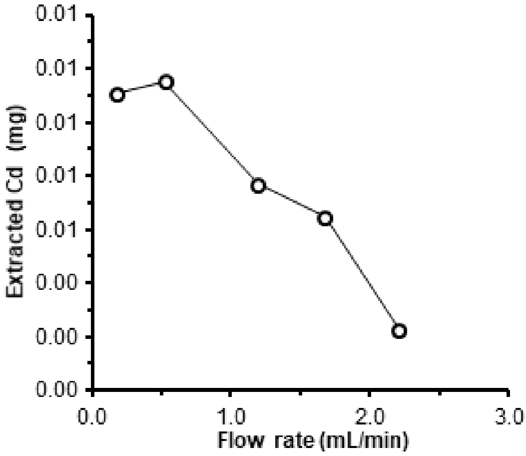

Fig 6. Influence of eluent flow rate on the extraction of Cd(II) on IIP

Table 1. Recovery of Cd(II) from solution samples after its SPE extraction on IIP (sample pH: 6; flow rate: 0.5 mL min^{-1}; elution: 2 mL of 1 mol L^{-1} HNO_3)

No.	Added Cd (mg L^{-1})	Found Cd (mg L^{-1})	Recovery (%)
1	0.010	0.00966	96.60
2	0.020	0.01912	95.60
3	0.030	0.02882	96.07
4	0.040	0.04040	101.00
5	0.050	0.04964	99.28
	Average		97.75
	RSD (%)		2.32

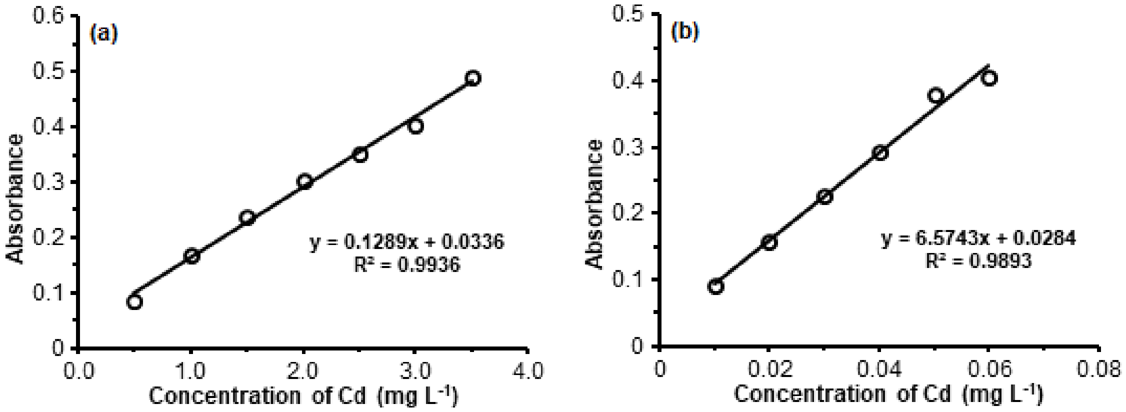

Fig 7. Calibration graph of Cd(II) solution (a) without preconcentration and (b) with 50-fold theoretical preconcentration

in Fig. 7. The LOD and LOQ obtained were 4.5 and 15 µg L^{-1} for without preconcentration, 0.5 and 1.67 µg L^{-1} for with 50-fold theoretical preconcentration. Application of the proposed method on the analysis of Cd(II) in an aqueous solution is presented in Table 1. Analytical recovery was assessed by analyzing fifth replicates of cadmium standard solution 0.01–0.05 mg L^{-1} and preconcentration by SPE. The analytical recovery obtained was 97.75%.

■ CONCLUSION

The new adsorbent IIP for the analysis of Cd(II) by SPE-FAAS has been synthesized through a precipitation polymerization process using 8-hydroxyquinoline as a complexing ligand, methacrylic acid as a monomer and ethylene glycol dimethacrylate as a crosslinker. Ethanol-acetonitrile (2:1) was used as a porogen, and benzoyl peroxide was used as an initiator. The optimized procedure consists of a sample loading (sample pH of 6) through IIP-SPE columns containing 100 mg of the IIP at a flow rate of 0.5 mL min^{-1}. Elution of Cd(II) from IIP was performed by passing 2 mL of 1 mol L^{-1} HNO_3. The LoD and LoQ obtained were 0.5 and 1.67 µg L^{-1} for with 50-fold theoretical preconcentration. The accuracy of the method of SPE-FAAS was 97.75%.

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