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Novel Imprinted Polymer for the Preconcentration of Cadmium with Determination by Inductively Coupled Plasma Mass Spectrometry

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Abstract

A novel Cd(II)-imprinted polymer was prepared with chemical immobilization approach by using N-methacryloyl-L-histidine as a vinylated chelating agent for on-line solid phase extraction of Cd(II) for determination by inductively coupled plasma mass spectrometry. Cd(II)-monomer complex was synthesized and copolymerized via bulk polymerization method in the presence of ethyleneglycoldimethacrylate cross-linker. The resulting polymer was leached with 1.0 mol L⁻¹ HNO₃ to generate the cavities in the polymer for Cd(II) ions. The experimental conditions, including load pH, solution flow rate, and eluent concentration for effective sorption of Cd(II) were optimized using a minicolumn of the imprinted polymer. A volume of 5.0 mL sample 5 µg L⁻¹ Cd(II) solution at pH 6.5 was loaded onto the column at 2.0 mL min⁻¹ by using a sequential injection system (FIAB 3200) followed by elution with 1.0 mL of 0.75 mol L⁻¹ HNO₃. The relative selectivity coefficients of the imprinted polymer for Cd(II) were 38.5, 3.5, 3.0, 2.5 and 6.0 in the presence of Cu(II), Ni(II), Zn(II), Co(II) and Pb(II), respectively. Computational calculations revealed that the selectivity of the imprinted polymer was mediated by the stability of Cd(II)-N-methacryloyl-L-histidine complex which was far more stable than those of commonly used monomers, such as 4-vinyl pyridine, methacrylic acid and vinylimidazole. The detection limit (3s) and relative standard deviation (%) were found to be 0.004 µg L⁻¹ and 3.2%, respectively. The method was validated by analysis of seawater certified reference material (CASS-4) and successfully applied to the determination of Cd(II) in coastal seawater and estuarine water samples.

Keywords

Cadmium; Ion-imprinted polymer; Chemical immobilization; Solid phase extraction; Inductively coupled plasma mass spectrometry

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Introduction

Cadmium (Cd) is recognized as an extremely significant pollutant due to its high toxicity and large solubility in water. It is among the 13 toxic metal species on the priority pollutant list of the Environmental Protection Agency (Pinto et al. 2004; Lu and Yan 2004). It has been classified as a carcinogen (Group IA) by International Agency for Research on Cancer (Behbahani et al. 2013). Cadmium is introduced to the environment in large quantities mainly from anthropogenic sources, including discharges of plating industry and smelters, power stations and waste batteries (Sanita and Gabbrielli 1999). Exposure to cadmium has been proved to have adverse effects on heart, lungs, bones and especially kidneys. Cadmium accumulates in kidneys and damages its filtering function. It is excreted very slowly from the body that may last 20–30 years (Wexler 2005; Patnaik 2007). Development of reliable and accurate analytical methods for monitoring and detection of trace amount of Cd ions in environmental, biological and food samples is of particular importance to protect the exposure of humans and animals to this extremely toxic element.

Several analytical techniques including flame atomic absorption spectrometry (FAAS) (Yilmaz and Kartal 2012), graphite furnace atomic absorption spectrometry (GFAAS) (Yang et al. 2009), inductively coupled plasma optical emission spectrometry (ICP-OES) (Silva, Roldan, and Gine 2009) and inductively coupled plasma mass spectrometry (ICP-MS) (Zereen, Yilmaz and Arslan 2014) have been used for determination of Cd in different samples. Today, ICP-MS has been considered the most powerful technique owing to its sensitivity, multi-element and isotope measurement capability, and wide linear dynamic range. Nonetheless, the direct analysis of real-world samples, especially those containing large amount of salts, by ICP-MS is challenging because of numerous adverse effects of saline samples on ICP-MS measurements, which span from multitude of spectral and non-spectral interferences to degradation of instrument lifetime (Huang and Beauchemin 2003; McCurdy and Woods 2004). Spectral and non-spectral interferences in ICP-MS can be minimized using high-resolution ICP-MS, collision/reaction cell ICP-MS and some analytical strategies such as standard additions method, isotope dilution, matrix matching and internal standardization. However, these techniques are costly and are not applicable to solve problems and they still suffer from matrix effects when samples are analyzed directly (McCurdy and Woods 2004, Salazar et al. 2011). Therefore, a sample pretreatment step for eliminating the saline matrix components and extracting the analyte(s) of interest remains very attractive in ICP-MS measurements.

Solid phase extraction (SPE) is a relatively fast and cost effective sample pretreatment approach as it allows preconcentration of analyte ion and removal of salt matrix simultaneously (Camel 2003). Selectivity, stability and efficiency of the solid support for extracting analyte ion and removal of matrix ions are critical in SPE applications. For this purpose, various functionalized polymeric sorbents and highly cross-linked polymers have been developed as selective SPE sorbents to enhance the selectivity in preconcentration of trace metal ions (Pereira and Arruda 2003; Rao, Daniel and Gladis 2004). Ion imprinted polymers are a class of novel polymeric sorbents developed for selective SPE of target metal ions from complex samples (Daniel, Rao and Rao 2005; Branger, Meouche and Margaillan 2013, Barciela-Alonso et al. 2014). Besides improved selectivity, ion imprinted polymers

offer high surface area, extended stability and reusability for affordable SPE analyses (Liu et al. 2011). In general, the synthesis of ion imprinted polymers consists of three stages: (i) complexation of the target metal ion (template) with appropriate ligand/s or functional monomers, (ii) copolymerization of the monomers around the template using a cross-linking agent, and (iii) removal of the target metal ion from the polymer yielding cavities or “imprinted sites” that are complementary in size and shape of imprint metal ion. Thus, the resultant polymer possesses improved selectivity to the template over the other ions in sample solution (Yilmaz et al. 2014).

Ion imprinted polymers prepared by chemical immobilization of vinylated ligands in the polymer matrix are advantageous for improved recognition by arranging the functional monomers around a template during polymerization (Candan et al. 2009; Firouzzare and Wang 2012; Tobiasz et al. 2009). The selectivity of the sorbent is largely influenced by the choice of complexing ligand, while the coordination geometry, coordination number of the metal ion, and the charge and size of the ion also affect the selectivity of ion imprinted polymers (Turjel and Esteban 2010; Pustam and Alexadratos 2010). To date, various ion imprinted polymers have been reported for separation and determination of transition metal ions, including Cd(II) (Andaç, Say and Denizli 2004; Li et al. 2011; Singh and Mishra 2009; Segatelli et al. 2010; Liu et al. 2004; Fan et al. 2012; Li et al. 2015, Panjali et al. 2015) Cu(II) (Yilmaz et al. 2014; Say et al. 2003; Yilmaz, O. Hazer and Kartal 2013; Shamsipur et al. 2010), Ni(II) (Ersöz, Say and Denizli 2004; Otero-Romaní et al. 2009), Zn(II) (Roushani et al. 2015; Shamsipur et al. 2014), Pb(II) (Zhu et al. 2009), Fe(III) (Saatcilar et al. 2006), Cr(III) (Birlik et al. 2007), and Hg(II) (Fan 2006).

L-histidine is an essential amino acid that is required for the production of histamine (Remko, Fitz and Rode 2010). It is one of the strongest metal coordinating ligands among the aminoacids and plays an important role in the binding of metal ions by proteins. L-Histidine has three potential metal-binding sites, carboxylate oxygen (O_{carboxyl}), imidazole imidonitrogen (N_{im}) and aminonitrogen (N_{am}) (Deschamps et al. 2005). The N-methacryloyl-(L)-histidine (or 2-methacrylamidohistidine) monomer bearing the L-histidine group was used for preparing ion imprinted polymers for Cu(II) (Say et al. 2003) and Ni(II) (Ersöz, Say and Denizli 2004). Yet, there is no literature regarding successful synthesis of an imprinted polymer of N-methacryloyl-(L)-histidine for Cd(II). In this study, we report the synthesis of a novel Cd(II)-imprinted polymer with vinylated chelating agent of N-methacryloyl-(L)-histidine through chemical immobilization. The Cd(II)-monomer complex was co-polymerized with ethylene glycol dimethacrylate cross-linker in the presence of 2,2'-azobisisobutyronitrile. The Cd(II)-imprinted polymer was used as a column packing to develop a SPE-ICP-MS method determination of Cd(II) after removal of Cd(II) from the polymer. The experimental parameters affecting the sorption efficiency of Cd(II) from aqueous solutions were optimized using sequential injection system (FIALab 3200). The analytical performance of the imprinted polymer, including, selectivity and capacity were evaluated under saline conditions with respect to non-imprinted polymer.

Experimental

Reagents and materials

Double deionized water (18.0 MΩ cm) was used for preparation of solutions. Multielement stock solutions of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were prepared from a 1000 µg mL⁻¹ stock standard solutions (Spextirep, Metuchen, NJ) in 5% (v/v) HNO₃ (Trace metal grade, Fisher Scientific). Ammonium acetate solution was prepared with 182 mL of trace metal grade ammonium hydroxide (NH₄OH, Fisher Scientific) and 112 mL of acetic acid (99.99+%, Sigma Aldrich) in 1.0 L deionized water. The pH of the solution was adjusted to pH 9.0 with NH₄OH and then used for adjusting the pH of the experimental solutions to desired pH. Ethyleneglycoldimethacrylate, methacryloyl chloride and CdCl₂·H₂O (Sigma Aldrich, St. Louis, MO) and L-histidine (Fisher Scientific, NJ) were used as received. 2,2-Azobisisobutyronitrile (Acros Organics) was purified by successive crystallizations from chloroform-methanol mixture. High purity salts of the Ca, Mg, Na and K were used to prepare matrix solutions.

Instrumentation

Measurements were performed by using a Varian 820MS inductively coupled plasma mass spectrometer (Varian, Australia). The instrument was equipped with a peltier-cooled double-pass glass spray chamber, a teflon Ari-mist nebulizer (SCP Science, Champlain, NY), quartz torch, Ni sampler and skimmer cones and all-digital detector. Samples were introduced manually. The instrument was optimized daily for sensitivity, doubly charged ions (<1%) and oxides (<3%) with 5.0 µg L⁻¹ ¹³⁸Ba, ²⁵Mg, ¹¹⁵In, ¹⁴⁰Ce, ²⁰⁸Pb solution. Data collection was achieved by ICP-MS Expert software package (version 2.2 b126). The operating parameters of the instrument are summarized in Table 1. Germanium (⁷²Ge) and rhodium (¹⁰³Rh) were used as internal standard elements to correct for possible instrumental drift and sensitivity changes. ⁷²Ge was used for Co, Ni, Cu, Zn while ¹⁰³Rh was assigned to Cd and Pb. The internal standard solution (5.0 µg L⁻¹ Ge and Rh in 1% v/v HNO₃) was mixed on-line with the sample solution. Two isotopes of the multi-isotopic elements, namely ⁶³Cu and ⁶⁵Cu for Cu, ⁶⁶Zn and ⁶⁸Zn for Zn, ⁶⁰Ni and ⁶²Ni for Ni, ¹¹¹Cd and ¹¹⁴Cd for Cd, and ²⁰⁶Pb and ²⁰⁸Pb for Pb were monitored during the course of the method optimization and analysis solutions. The pH of the solutions was adjusted by using an Oakton digital pH meter with glass electrode (Model 510).

The NMR (Nuclear magnetic resonance, ¹H) spectrum of the monomer was recorded by a Varian Unity Inova 500 MHz FT-NMR spectrometer (Australia) using deuterium oxide (D₂O) as solvent and tetramethylsilane as internal standard. Infrared spectra of the monomer, monomer-Cd complex, imprinted and non-imprinted polymers were recorded using a Nexus, Model 470 infrared spectrometer. Elemental analysis was performed by an ECS 4010 analytical platform (Costech instruments, USA).

Preparation of Cd(II)-imprinted polymer

Synthesis of N-methacryloyl-L-histidine and complexation with Cd(II)—N-methacryloyl-L-histidine was synthesized according to previously reported procedures by Say (Say et al. 2003) and Lele (Lele, Kulkarni and Mashelkar 1999) with some

modifications. Briefly, 5.0 g of L-Histidine and 0.2 g NaNO_2 were dissolved in 30 mL of 5% (v/v) K_2CO_3 aqueous solution of saturated K_2CO_3 solution. This solution was cooled down to 0 °C in an ice bath. Then 4.0 mL of methacryloylchloride was added slowly into this solution under nitrogen atmosphere and stirred magnetically at room temperature for 2 h. At the end of the reaction period, the pH of the solution was adjusted to 7.0 and the unreacted components and reaction impurities were extracted with ethylacetate. Aqueous phase containing the monomer was evaporated in a rotary evaporator. The residue was further extracted into 10 mL of methanol yielding a turbid solution (salts and soluble ligands). This solution was filtered to remove salts (e.g., KCl and K_2CO_3). Clear methanol solution with ligands was obtained and added into absolute acetone (e.g., 750 mL) to reprecipitate the product (e.g., monomer). This step was repeated twice to purify the monomer, and then the product (N-methacryloyl-(L)-histidine) was vacuum-dried overnight. The yield was 48%.

The monomer was characterized with infrared spectroscopy and ^1H NMR. The following characteristics bands were obtained by infrared spectroscopy: 3387 cm^{-1} (-NH stretching), 1707 cm^{-1} (acid carbonyl) (Lele, Kulkarni and Mashelkar 1999), 1654 cm^{-1} (amide carbonyl), 1592 cm^{-1} (-NH bending). ^1H NMR obtained in D_2O revealed peaks (δ in ppm) at 1.82 (s, 3H, $-\text{C}=\text{C}-\text{CH}_3$), 2.95–3.14 (m, 2H, $-\text{C}-\text{CH}_2$ -imidazole), 4.42–4.45 (q, H, $-\text{CH}-\text{COOH}$), 5.35 (s, 1H, $-\text{CH}_a=\text{C}-$), -5.56 (s, 1H, $-\text{CH}_b=\text{C}-$), 6.92 (s, 1H imidazole, $-\text{C}=\text{CHN}-$), 7.79 (s, 1H imidazole, $-\text{N}=\text{CHNH}-$).

For the synthesis of Cd(II)-N-methacryloyl-(L)-histidine complex, 2.0 mmol (0.892 g) of N-methacryloyl-(L)-histidine was dissolved in 20 mL ethanol. A 1.0 mmol (0.366 g) CdCl_2 dissolved pure 10 mL ethanol was added slowly into this solution with continuous stirring at room temperature. The reaction solution was stirred for 6 h. The solvent was removed and the white solid was washed with a mixture of ethanol and acetonitrile. The yield was 0.904 g (72%). The decomposition temperature of the complex was measured to be higher than 260 °C. The infrared spectrum showed peaks at 3297 cm^{-1} (N-H stretching), 3125 cm^{-1} (C-H aromatic), 2982 and 2921 cm^{-1} (C-H aliphatic), 1654 cm^{-1} (C=O amide) and 1573 cm^{-1} (N=C-). The FT-IR spectra of the N-methacryloyl-(L)-histidine and Cd(II)- N-methacryloyl-(L)-histidine complex are compared in Figure 1. The peak corresponding to imidazole ring ($-\text{C}=\text{N}-$) and amide N (-NH) in N-methacryloyl-(L)-histidine at 1592 cm^{-1} shifted to 1573 cm^{-1} in Cd(II)- N-methacryloyl-(L)-histidine suggesting coordination of the imidazole ring-N and amide N with the Cd(II). The stretching frequency assigned to acid carbonyl (COOH) at 1707 cm^{-1} in MAH disappeared in the Cd(II)-monomer. This pattern is also reported for other metal-amino acid complexes (Chohan et al. 2006). These data suggest that the imidazole ring N, amide N and carboxylate O are involved in coordination with the Cd(II) in the Cd(II)-N-methacryloyl-(L)-histidine complex depicted in Figure 2. The elemental composition was calculated to be $\text{C}_{20}\text{H}_{24}\text{N}_6\text{O}_8\text{CdCl}_2$: 38.27% C, 3.85% H, 13.39% N, 17.91% Cd. The experimentally determined values were 38.58% C, 4.05% H, 13.95% N, and 17.32% Cd.

Preparation of Cd(II)-imprinted polymer and non-imprinted polymer

The synthesis of poly(Ethyleneglycoldimethacrylate-N-methacryloyl-(L)-histidine/Cd(II)) particles was performed by bulk polymerization method as described below. About 1.0

mmol (0.628 g) Cd(II)-monomer complex was dissolved in 10 mL dimethylsulfoxide. To this solution, 8 mmol ethylene glycoldimethacrylate (1.6 mL) cross-linker and 0.05 mmol 2,2'-azobisisobutyronitrile (16 mg) free radical initiator were added. Nitrogen gas was purged into the solution for 5 min under stirring and then the reaction vial was sealed and kept at 70 °C for 12 h. The resulting light yellow material was transferred to another vial, thoroughly washed with water and dried at 60 °C for 24 h. The blocks of the polymer were ground and sieved to obtain a powdered material of 90–180 µm. The polymeric particles were washed with 0.5 mol L⁻¹ HNO₃ several times to completely remove Cd(II) from the resin and finally with water to neutralize the particles. The resulting polymeric particles (i.e., Cd(II)-free imprinted polymer) were dried at 60 °C. Non-imprinted polymer was prepared similarly with N-methacryloyl-(L)-histidine and ethylene glycoldimethacrylate. A schematic representation for the preparation of Cd(II)-imprinted polymer and the processes of sorption and desorption of Cd(II) ions are illustrated in Figure 2.

Solid phase preconcentration system and optimization of SPE conditions

SPE columns were made from 2-cm long teflon tubing (0.4 cm i.d.) which were packed with 30 mg of imprinted and non-imprinted polymers. Both ends of the columns were closed with glass wool to retain the packing material. For cleaning, each column was washed with 0.5 mol L⁻¹ HNO₃ and deionized water, respectively. A FIALab 3200 (FIALab Instruments Inc., Bellevue, WA) sequential injection unit was used for automated solid phase preconcentration. The system was controlled by the FIALab software package (version 5.0) running on a personal computer. The FIALab 3200 was operated during SPE studies using a program described in a previous study (Zereen, Yilmaz and Arslan 2014).

For optimization of load pH, the pH of the sample solutions was varied from pH 3 to 9 for 5 µg L⁻¹ Cd(II) solutions (as multielement). A volume of 5 mL solution with appropriate pH was loaded onto the columns packed with the resins of imprinted polymer and non-imprinted polymer at 2.0 mL min⁻¹ and eluted with 1.0 mL of 0.75 mol L⁻¹ HNO₃. The concentration of HNO₃ solution was varied from 0.15 to 0.9 mol L⁻¹ HNO₃ to find the optimum elution conditions. The effect of flow rate on sorption efficiency was examined at the optimum pH for 5 µg L⁻¹ multielement solution by increasing the flow rate of sample solution from 0.5 to 5 mL min⁻¹.

Sample preparation

The accuracy of the procedure was verified by determination of Cd in certified reference materials of seawater (CASS-4) and estuarine water (SLEW-3). The procedure was then applied to the determination of Cd from coastal seawater and estuarine water samples. Coastal seawater was collected in summer of 2014 from the Pensacola Bay, FL. Estuarine water samples were collected from the Grand Bay Estuarine Research Reserve in the northern Gulf of Mexico along the coast of Mississippi. The water samples were placed into acid-cleaned polypropylene bottles and acidified to 0.15 mol L⁻¹ HNO₃ at the sampling site. At the laboratory, they were filtered through 0.45-µm membrane filters and stored in 0.15 mol L⁻¹ HNO₃ until analysis. The pH of the sub-samples was adjusted to pH 6.5 with the ammonium acetate solution and the proposed method was applied to the samples.

Selectivity experiments

In order to investigate the selective sorption behavior of Cd(II)-imprinted polymer to Cd(II) ion, competitive sorption tests were conducted with Ni(II), Co(II), Pb(II), Cu(II) and Zn(II) ions that possess same charge and similar ionic radii. About 20 mg of Cd(II) ion-imprinted polymer or non-imprinted polymer was added into 10 mL of binary metal mixture solutions of Cd(II)/Ni(II), Cd(II)/Cu(II), Cd(II)/Co(II), Cd(II)/Pb(II) and Cd(II)/Zn(II) containing 10 mg L⁻¹ of above each individual metal ion at pH 6.5 for sorption equilibrium. The concentration of metal ions remained in solution was determined by ICP-MS. The distribution ratio (D), selectivity coefficient (k) and the relative selectivity coefficient (k') were calculated as the following equations (Li et al. 2015):

$$D = \frac{(C_i - C_e)}{C_e} \times \frac{V}{W} \quad (1)$$

$$k = \frac{D_{\text{Cd}}}{D_{\text{M}}} \quad (2)$$

$$k' = \frac{k_{\text{IIP}}}{k_{\text{NIP}}} \quad (3)$$

where C_i and C_e are the initial and equilibrium concentrations (mg L⁻¹) of metal ions of Cd(II), Ni(II), Cu(II), Co(II), Pb(II) or Zn(II)). V is the volume of the solution (mL), W is the mass used of sorbent (g). D_{Cd} and D_{M} represent the distribution ratio of Cd(II) ion and other metal ions, respectively. $k_{\text{imprinted polymer}}$ and $k_{\text{non-imprinted polymer}}$ are selectivity coefficients of the imprinted and non-imprinted polymers, respectively.

Evaluation of sorption capacity

In order to investigate the sorption capacity of Cd(II)-imprinted polymer and non-imprinted polymer to Cd(II), about 20 mg of appropriate sorbent and 10 mL of Cd(II) solution at pH 6.5 with varying initial concentrations (from 0 to 60 mg L⁻¹) were placed into 50-mL screw capped conical test tubes. The tubes were shaken for 30 min on an oscillating shaker. Then, the concentration of Cd(II) remained in solution (e.g., unadsorbed Cd) was measured by ICP-MS.

Results and discussion

Characterization of Cd(II) ion-imprinted polymer

The imprinted and non-imprinted polymers prepared were characterized by infrared spectroscopy. The infrared spectra of the (A) unleached, (B) leached and (C) non-imprinted polymers are presented in Figure 3. As expected, all of the polymers exhibited similar spectral profiles. The similarities between the infrared spectra of unleached, leached and

non-imprinted materials suggested that the leaching process did not affect the polymer network. The two peaks at about 2950 and 2987 cm^{-1} can be associated with C–H stretching of $-\text{CH}_2-$ and $-\text{CH}_3$ groups in the polymeric chain, respectively. The intense adsorption band at 1720 cm^{-1} was assigned to carbonyl groups from ethylene glycoldimethacrylate. The C–O vibration was observed at 1144 cm^{-1} . The absorption at 1630 cm^{-1} is associated with C=C and C=N (ring) stretching.

Selectivity of the Cd(II)-imprinted polymer and non-imprinted polymer

Competitive sorption experiments of Cd(II)/Ni(II), Cd(II)/Cu(II), Cd(II)/Co(II), Cd(II)/Pb(II) and Cd(II)/Zn(II) from their binary mixture were carried out in the batch system to verify the selectivity of the Cd(II)-imprinted polymer relative to non-imprinted polymer. The results are provided in Table 2. The distribution ratio of Cd(II)-imprinted polymer for Cd(II) was significantly higher than that of non-imprinted polymer. The relative selectivity coefficients of Cd(II)-imprinted polymer were 38.5, 3.5, 2.5, 6.0 and 3.0 against Cu(II), Ni(II), Co(II), Pb(II) and Zn(II), respectively. Although the L-histidine which was used for the preparation of N-methacryloyl-(L)-histidine monomer has a strong complexation affinity for Cu(II) ion (Sigel and McCormick 1971), the Cd(II)-imprinted polymer prepared had a superior binding selectivity (k' 38.5) for the Cd(II) ion in the binary system of Cd(II)/Cu(II). These results indicated that Cd(II)-imprinted polymer possessed substantial selectivity in the competitive environment for Cd(II), which is due to the ion imprinting effect producing sites matched with size and geometry of Cd(II).

Optimization of SPE conditions

Effect of pH on sorption of Cd(II) on imprinted and non-imprinted polymer—

The functionalized ligand, N-methacryloyl-(L)-histidine, is chemically immobilized in the polymeric network of both imprinted polymer and non-imprinted (see Figure 2). The Cd(II) ions are retained on the polymeric support by complexing with N-methacryloyl-(L)-histidine. Therefore, the formation of a complex between Cd(II) and N-methacryloyl-(L)-histidine is expected to be influenced by the pH of solution. The effect of pH on the sorption of Cd(II) in multielement standard solution ($5 \mu\text{g L}^{-1}$) is illustrated in Figure 4 from pH 3 to 9. Maximum recovery was 78% for non-imprinted polymer at pH 7 in the absence of any matrix, which was indicative of weak sorption of Cd(II) by non-imprinted polymer. The retention of Cd(II) on the imprinted polymer took place within a range from pH 6 to pH 7 where recoveries ranged from 98% (pH 6) to 101% (pH 7). A pH of 6.5 was optimum to achieve quantitative preconcentration and examination of analytical merits of imprinted polymer in the subsequent studies.

Optimization of eluent acid concentration and flow rates

During preliminary studies, dilute solutions of HNO_3 (e.g., 5% v/v HNO_3) were found sufficient for cleaning the column and removing the retained Cd(II). Thus, all elution studies were carried by varying the concentration of HNO_3 solutions from 0.15 to 0.9 mol L^{-1} . About 86% of Cd(II) was recovered when elution was performed with 1.0 mL of 0.15 mol L^{-1} HNO_3 . The recoveries were improved to 98% for 1.0 mL of 0.6 mol L^{-1} HNO_3 (ca. 4% v/v HNO_3) indicating that a minimum of 0.6 mol L^{-1} was required to remove Cd(II) from the column quantitatively. The recoveries with 0.9 mol L^{-1} HNO_3 were around 99–101%,

and were not significantly different from that for 0.6 mol L⁻¹. A solution of 0.75 mol L⁻¹ HNO₃ (5% v/v HNO₃) was chosen as the optimum eluent. Elutions with different volumes (e.g., 0.5 to 2 mL) of 0.75 mol L⁻¹ HNO₃ showed that a volume of 1.0 mL was adequate to ensure effective cleaning of the column.

The flow rate of the sample solution is an important parameter in flow-based SPE procedures as it determines the extent of interaction of analyte ion with the imprinted sites on the column. The recoveries for Cd(II) varied between 101% and 98% when the flow rate of the solution increased from 0.5 to 3.0 mL min⁻¹ indicating that Cd(II) was retained by the column of Cd(II)-imprinted polymer at up to 3.0 mL min⁻¹. At higher flow rates, the recovery was less than 95% and gradually decreased to 88% at 5 mL min⁻¹ because of the insufficient contact of Cd(II) with the sorbent. A flow rate of 2.0 mL min⁻¹ was chosen as optimum for column procedures. The flow rate of the eluent did not affect the recoveries; elution of Cd was successful even at 5.0 mL min⁻¹. Yet, the flow rate of the HNO₃ eluent was kept at 2.0 mL min⁻¹ for efficient cleaning of the column and smooth operation of the FIALab 3200 system.

Matrix effects

The effects of potential matrix ions of alkaline and alkaline earth elements, Na(I), K(I), Mg(II), Ca(II), and transition and heavy metals, Cu(II), Zn(II), Ni(II), Fe(III), Mn(II), Pb(II), were examined individually. The recoveries for 5.0 µg L⁻¹ Cd(II) are summarized in Table 3. The presence of interfering matrix ions had no significant influence on the sorption of Cd(II) under the optimized operating conditions. This result also indicated that Cd(II)-imprinted polymer possessed good selectivity for Cd(II). In concentrated Ca(II) and Mg(II) solutions (see Table 3), the residual Ca(II) and Mg(II) concentrations measured in 1 mL analysis solutions were about 6 and 15 µg mL⁻¹ (ppm) that indicated that the imprinted polymer allowed removal of heavy salt matrix very effectively.

Theoretical considerations

Computational approaches are increasingly applied to assist in the design of molecularly imprinted polymers as they provide mechanistic insights into the molecular recognition and stability of the analyte-ligand complexes. Ideally, the functional monomer that possesses the lowest binding energy towards the template should produce the polymer with the highest affinity (Piletsky et al. 2001). Thus, in this work, free-energy calculations were performed to elucidate the affinity of N-methacryloyl-(L)-histidine to Cd(II), in comparison to several commercially available monomers. They include 1-vinylimidazole, N-vinylpyrrolidone, 4-vinylpyridine, methacrylamide, methacrylic acid, methyl methacrylate and 2-hydroxyethyl methacrylate. All calculations were performed using the Gaussian 09 software. The density functional theory with B3LYP(Becke, three-parameter, Lee-Yang-Parr) and LanL2MB basis set were applied to obtain optimal geometries of all investigated species. The geometry characterized by minimum energy (E) was used for the metal-ligand complex calculations. The binding energies (E) were calculated by using the equation below and the results are summarized in Table 4.

$$\Delta E = E(\text{template-monomer complex}) - E(\text{template}) - E(\text{monomer}) \quad (4)$$

The binding energy for Cd(II)-N-methacryloyl-(L)-histidine complex was $-342.0 \text{ kcal mol}^{-1}$ which was the lowest in comparison to Cd(II) complexes of the other ligands. This indicates that N-methacryloyl-(L)-histidine interacts the most strongly with Cd(II), while the interaction between methyl methacrylate and Cd(II) is the weakest ($E = -185.1 \text{ kcal mol}^{-1}$). Based on these results, it is expected that successful preparation of a polymer utilizing N-methacryloyl-(L)-histidine would yield a chelating support surface of high affinity to Cd(II). The selectivity of the polymer could further be improved against matrix ions via imprinting approach (e.g., polymerization of Cd(II)-N-methacryloyl-(L)-histidine) as it produces size-wise compatible chelating surfaces for Cd(II).

Sorption capacity and isotherm

The sorption capacity is an important factor in elucidating the analytical merit of the sorbent material. The data regarding the sorption capacities (q_e , mg g^{-1}) of the imprinted and non-imprinted polymer are shown in Figure 5 as a function of the initial Cd(II) concentration in the solution. The mass of Cd per gram of the polymer (q_e , mg g^{-1}) increased with increasing concentrations of Cd(II) (C_i , mg L^{-1}) up to about 30 mg L^{-1} Cd(II), then levelled off. The maximum sorption capacity of the Cd(II)-imprinted polymer was calculated to be 13.8 mg g^{-1} , which was substantially higher than that of non-imprinted polymer (3.82 mg g^{-1}), which is an indication of the fact that imprinted polymer possessed more size-matching binding sites for Cd(II) than that of non-imprinted polymer.

The data in Figure 5 for the sorption of Cd(II) on the imprinted polymer was fitted to the Langmuir's isotherm equation in the linearized form as shown below,

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \left(\frac{1}{q_m} \right) C_e \quad (5)$$

where C_e is the equilibrium concentration (mg L^{-1}) of Cd(II) in the solution, b is a constant of the Langmuir model (L mg^{-1}), and q_m is the maximum sorption capacity of the Cd(II)-imprinted polymer (mg g^{-1}). The plot of C_e/q_e against C_e yields a straight line (see Figure 6) and the values of q_m and b can be calculated from the slope and intercept of the plot, respectively. As shown in Figure 6, Langmuir sorption plots for Cd(II) obtained by the least-squares method are well-fitted with the Langmuir's equation ($r^2 = 0.9996$) suggesting the sorption of Cd(II) follows the formation of monolayer coverage of Cd(II) at the surface of the sorbent.

Column stability

To examine the stability of the resin, a total of 10 loading and elution cycles were performed using the same column under the optimum conditions (e.g., pH, 6.5 and 1.0 mL of $0.75 \text{ mol L}^{-1} \text{ HNO}_3$ eluent). No significant changes were observed in the retention performance of the column. Mean recovery was $97.6 \pm 4.1\%$.

The performance characteristics of the Cd(II)-imprinted polymer are compared in Table 5 with other Cd(II)-imprinted polymers reported in the previously. The Cd(II)-imprinted polymer developed in this work exhibits high affinity, sorption capacity and excellent recognition ability. In comparison to the other imprinted polymers, the Cd(II)-imprinted polymer also possesses better selectivity over Cu(II) ($k' = 38.5$).

Figures of merit and method validation

External calibration was performed with 0, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10 $\mu\text{g L}^{-1}$ aqueous multielement standard solutions. The calibration standards were preconcentrated using the optimized procedure. Signals from five standard solutions that bracket that of samples were used to calculate Cd(II) concentration in the samples ($r^2 = 0.997 - 0.999$). To determine the limit of detection, 5 mL blank solution ($n = 12$) at pH 6.5 was passed through the column and eluted with 1 mL of 0.75 mol L^{-1} HNO_3 . A limit of detection (3s method) of 0.004 $\mu\text{g L}^{-1}$ was achieved. The relative standard deviation was 3.2% for preconcentration of 1.0 $\mu\text{g L}^{-1}$ Cd(II) standard solution.

The method was validated by analysis of seawater (CASS-4) and estuarine water (SLEW-3) certified reference materials. Four replicate samples ($n=4$) were analyzed for each certified reference material. Experimental concentrations measured in the certified reference materials were consistent with the certified values within the 95% confidence level (Table 6). These results are also consistent with those provided in Table 3 verifying the ability of the imprinted polymer to quantitatively extract Cd(II) from high Na, K, Ca and Mg matrices. For determination of Cd(II) in coastal seawater and estuarine water, spiked samples were preconcentrated and analyzed along with the unspiked water samples ($n=5$). Seawater samples were spiked with 0.1 $\mu\text{g L}^{-1}$ Cd(II) and the estuarine waters were spiked with 0.5 $\mu\text{g L}^{-1}$ Cd(II). The concentration of Cd(II) was 0.022 $\mu\text{g L}^{-1}$ in coastal seawater and 0.42 $\mu\text{g L}^{-1}$ in estuarine water. Mean recoveries were 97% in seawater and 94% in estuarine water.

Conclusions

In this study, we have synthesized a new ion-imprinted polymer incorporating N-methacryloyl-L-histidine as a vinylated chelating monomer via chemically immobilization approach. Computational calculations showed that N-methacryloyl-L-histidine possessed strong affinity to Cd(II) over commercially available monomers. The Cd(II)- N-methacryloyl-L-histidine complex showed the lowest binding energy (e.g., highest stability); therefore, the, interaction energy between template metal ion and the monomer could be used for screening among a large list of monomers for preparing suitable imprinted polymers.

Experimentally, it was demonstrated that the imprinted polymer produced from Cd(II)- N-methacryloyl-L-histidine complex was highly selective toward Cd(II) against the common transition and heavy metal ions. The Cd(II)-imprinted polymer reported here possesses large capacity to achieve high enrichment factors in determination of Cd impurities or contamination from saline samples, such as seawater, and high purity materials. In addition, the Cd(II)- imprinted polymer is highly stable under acidic conditions (e.g., 0.75 mol L^{-1}

HNO₃) that is advantageous for extended use of the same column without experiencing any changes in its retention performance.

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Figure 1.
Infrared spectra of the (a) N-methacryloyl-(L)-histidine and (b) Cd(II)-N-methacryloyl-(L)-histidine complex.

Figure 2.
Schematic representation of the synthesis of Cd(II)-N-methacryloyl-(L)-histidine complex,
Cd(II)-imprinted polymer and associated sorption and desorption of the Cd(II) ions.

Figure 3.
Infrared spectra for the (A) unleached, (B) leached and (C) non-imprinted polymer.

Figure 4. The effect of solution pH on the retention of Cu(II) on the columns of Cd(II)-imprinted polymer and non-imprinted polymer.

Figure 5. Sorption isotherms for Cd(II) onto the Cd(II)-imprinted polymer and non-imprinted polymer ($n = 3$).

Figure 6. Langmuir plot for Cd(II) on Cd(II)-imprinted polymer ($y = 0.0722x + 0.022$, $R^2 = 0.9996$) ($n = 3$).

Table 1

Operating parameters for Varian 820-MS ICP-MS instrument.

RF Power (kW)	1.4
Plasma Ar flow (L min ⁻¹)	18
Auxiliary Ar flow (L min ⁻¹)	1.8
Nebulizer Ar flow (L min ⁻¹)	1.0
Sheath Ar flow (L min ⁻¹)	0.1
Sampling depth (mm)	6
Pump rate (rpm; mL min ⁻¹)	6; 0.2
Stabilization time (s)	20
Spray chamber temperature (°C)	3
Scan mode	Peak hopping
Dwell time (ms)	20
Points/peak	1
Scans/peak	3
Scans/replicate	3
Isotope	110,111

Table 2

Distribution ratios (mg L^{-1}), selectivity coefficients and relative selectivity coefficients for Cd(II)-imprinted polymer and non-imprinted polymer.

Binary system	Sorbent	Distribution ratio (Cd)	Distribution ratio (M)	selectivity coefficient	relative selectivity coefficient
Cd(II)/Cu(II)	Imprinted polymer	18611	10101	1.84	38.5
	Non-imprinted polymer	286	5987	0.048	
Cd(II)/Ni(II)	Imprinted polymer	8056	2113	3.81	3.5
	Non-imprinted polymer	712	655	1.08	
Cd(II)/Zn(II)	Imprinted polymer	11029	10363	1.06	3.0
	Non-imprinted polymer	662	1869	0.354	
Cd(II)/Pb(II)	Imprinted polymer	19112	886	21.5	6.0
	Non-imprinted polymer	4581	1266	3.61	
Cd(II)/Co(II)	Imprinted polymer	8992	650	13.8	2.5
	Non-imprinted polymer	4407	798	5.52	

M stands for the Cu, Ni, Zn, Pb or Co.

Table 3

The effect of foreign ions on the retention of $5 \mu\text{g L}^{-1}$ Cd(II). Values are average $\pm$ standard deviation for replicate samples (n = 3).

Interfering ion	Concentration (mg L ⁻¹)	Recovery (%)
Na(I)	10000	97.6 $\pm$ 1.7
K(I)	1000	101 $\pm$ 2.1
Ca(II)	1000	99.8 $\pm$ 1.0
Mg(II)	1000	97.4 $\pm$ 4.4
Zn(II)	5	95.6 $\pm$ 4.0
Cu(II)	5	96.5 $\pm$ 3.4
Ni(II)	5	95.4 $\pm$ 2.8
Co(II)	5	99.0 $\pm$ 4.5
Fe(III)	5	98.6 $\pm$ 4.3
Mn(II)	5	99.6 $\pm$ 5.2
Pb(II)	5	102 $\pm$ 3.5
Cr(III)	5	96.9 $\pm$ 3.6

Table 4

Predicted binding energy and total energies of components for the selected Cd-monomer complexes in gas phase. ($E_{\text{Cd(II)}} = -47.124$ au. 1 a.u.= 627.52 kcal/mol; Mulliken's atomic charge of the indicated atom).

Monomer	Energy of monomer (a.u.)	Energy of Cd-monomer complex (a.u.)	Binding energy(kcal mol ⁻¹)
N-methacryloyl-(L)-histidine	-768.751	-816.420	-341.998
1-Vinylimidazole	-301.558	-349.110	-268.579
N-Vinylpyrrolidone	-359.419	-406.915	-233.437
Methacrylamide	-282.889	-330.363	-219.632
2-Hydroxyethyl methacrylate	-454.308	-501.770	-212.102
4-Vinylpyridine	-321.636	-369.08	-202.689
Methyl methacrylate	-341.314	-388.737	-187.315
Methacrylic acid	-302.460	-349.879	-185.118

Table 5

Comparison of sorption characteristics of various Cd(II)-imprinted polymers.

Ligand/monomer	pH	Relative selectivity coefficient				Sorption capacity (mg g ⁻¹)	Reference
		Cu(II)	Ni(II)	Zn(II)	Pb(II)		
N-methacryloyl-(L)-cysteine methyl ester	7.0	N.R.	no reported	10.41	14.03	2.98	Andac, Say and Denizli (2004)
3-Thiocyanatopropyltriethoxysilane	6.0	6.7	no reported	11.6	8.9	44.7	Li et al. (2011)
2-(p-Sulphophenylazo)-1,8-dihydroxy-3,6 naphthalene disulphonic acid trisodium salt	6.0	6.6	no reported	7.4	no reported	0.27	Singh and Mishra (2009)
1-Vinylimidazole	6.8	4.44	no reported	1.38	157.5	4.56	Segatelli et al. (2010)
Diazoaminobenzene-4-vinylpyridine	6.0	51.2	no reported	45.6	no reported	10.4	Liu et al. (2004)
3-[2-(2-Aminoethylamino)ethylamino] propyltrimethoxysilane	6.0	6.17	14.02	3.0	3.12	57.4	Fan et al. (2012)
Allyl thiourea	5.0	2.86	6.42	11.50	9.46	38.30	Li et al. (2015)
N-methacryloyl-(L)-histidine	6.5	38.5	3.5	3.0	6.0	13.8	This work

Table 6

The elemental concentrations ($\mu\text{g L}^{-1}$) and recoveries for Cd from the analysis of Near shore seawater (CASS-4), estuarine water (SLEW-3) certified reference materials, and coastal seawater and estuarine water samples. Values are given as mean $\pm$ standard deviation of five replicate analyses for each sample. Spike concentrations are 0.1 and 0.5 $\mu\text{g L}^{-1}$ for coastal seawater and estuarine water samples, respectively.

Sample	Determined		Certified value	Recovery (%)
	Unspiked	Spiked		
Coastal seawater	0.022 $\pm$ 0.006	0.119 $\pm$ 0.008	–	97
Estuarine water	0.42 $\pm$ 0.01	0.89 $\pm$ 0.02	–	94
CASS-4	0.025 $\pm$ 0.009	–	0.026 $\pm$ 0.003	–
SLEW-3	0.049 $\pm$ 0.006	–	0.048 $\pm$ 0.004	–