

Polyurethane composite adsorbent using solid phase extraction method for preconcentration of metal ion from aqueous solution

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Abstract Polyurethane composite adsorbent polymeric material was prepared and investigated for selected solid-phase extraction for metal ions, prior to its determination by inductively coupled plasma optical emission spectrometry. The surface characterisation was done using Fourier transform infrared spectroscopy. The separation and preconcentration conditions of the analytes investigated includes influence of pH, sample loading flow rate, elution flow rate, type and concentration of eluents. The optimum pH for the highest efficient recoveries for all metal ions, which ranged from 70 to 85 %, is pH 7. The metal ions were quantitatively eluted with 5 mL of 2 mol/L HNO₃. Common coexisting ions did not interfere with the separation. The percentage recovery of the metal ions ranged between 70 and 89 %, while the results for the limit of detection and limit of quantification ranged from 0.249 to 0.256 and 0.831 to 0.855, respectively. The experimental tests showed good preconcentration results of trace levels of metal ions using synthesised polyurethane polymer adsorbent composite.

Keywords Heavy metals · Polymer adsorbent composite (PCAD) · Preconcentration · Solid phase extraction (SPE) · Inductively coupled plasma optical emission spectroscopy (ICP-OES)

Introduction

Analyses of both inorganic and organic compounds in environmental samples, especially waste and natural water samples, have been performed on a continuous basis in order to monitor and assess the level of environmental pollution associated with health issues which have been on the increase in recent times (Jain et al. 2003; Kocaoba and Akyuz 2005; Bulut and Tez 2007; Rezaei et al. 2009; Mittal et al. 2009; 2010; Rafati et al. 2010; Gupta et al. 2011a, b, c). Moreover, direct analysis of these inorganic compounds especially metal ions by atomic spectroscopy method, such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma optical emission spectroscopy (ICP-OES), and flame atomic absorption spectroscopy (FAAS), is often difficult due to the matrix interference and low concentration, and this make it difficult for the instrument to detect the ion which might be out of range of instrument's detection limit. Thus, a preconcentration method for the enrichment of these metal ions is necessary (Gupta et al. 2004; Kocaoba and Akyuz 2005; Alkan et al. 2008; Madrakian et al. 2008; Gupta et al. 2010).

Numerous preconcentration and separation techniques application have been reported for metal-ion analysis, which include cloud-point extraction (CPE) (Anthemidis et al. 2001, 2002), co-precipitation (Duran et al. 2009), electrochemical deposition (ECD) (Soylak and Tuzen

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2008), flotation (Pan et al. 2007), liquid–liquid extraction (LLE) (Candir et al. 2008), solid-phase extraction (SPE) (Otero-Romani et al. 2005; Elci et al. 2008; Huang et al. 2008; Chen et al. 2009), solid-phase microextraction (SPME) (Camel 2003; Chen et al. 2009), etc. However, SPE is the preferred method mainly due to its simplicity, direct application in microlitre (μL) volume, speed, minimal sample loss, higher preconcentration factor, rapid phase separation, cost and time saving (Bulut and Tez 2007; Chen et al. 2009; Mohammadi et al. 2011).

The SPE method is based on the principle of analyte transfer from the aqueous medium, i.e. phase, to the active sites on the solid phase of an adsorbent (Bulut and Tez 2007). Numerous technologies involving adsorbents have been applied as preconcentration adsorbents for metal ions, including alumina (Li et al. 2002; Absalan and Mehrdjardi 2003), activated carbon (AC) (Ensafi et al. 2003; Gupta et al. 2012a, b; Olorundare et al. 2012), C18 cartridge silica, chelex-100 (Ferri and Sangiorgio 1996), polyurethane foam (Ant-hemidis et al. 2002; Pinto et al. 2004), microcrystalline naphthalene (Candir et al. 2008; Elci et al. 2008), nanoparticles (Gupta and Nayak 2012; Sanghavi et al. 2013), silica gel (Akl et al. 2004), cyclodextrins CDs (Krause et al. 2010), zeolites (Ngah et al. 2012), and clay (Kiliaris and Papaspyrides 2010). However, the development of purification and extraction methods using these adsorbents for the enrichment of metal ions in environmental samples has been a challenge due to drawbacks which have limited their application for effective monitoring and curtailments of pollutants in the environment (Pinto et al. 2004; Alkan et al. 2008; Castro et al. 2011). Recently, there has been a growing interest in environmentally safe application of these adsorbent materials (Pinto et al. 2004, 2005). This is because most of these adsorbents, available in the market for environmental application, are either obtained in pellets or powder form (Pinto et al. 2004; Oprea 2011). The present form of these adsorbents' physical appearance hinders their optimum application in the water-treatment process. Furthermore, these factors have restricted the industrial application of these adsorbent materials, especially those applied in separation technology (Pinto et al. 2004, 2005). Apart from their physical properties, the regeneration of the spent adsorbent materials to their original state of adsorption capacity is a challenge because of its cost implication and heat-controlled environment required for their treatment (Gayatri and Ahmaruzzaman 2010). This operational drawback has raised questions of development of composite support materials that could be easily regenerated without the thermal energy input (Gayatri and Ahmaruzzaman 2010). An approach of mitigating a

solution to these drawbacks is production of an adsorbent material as a support in the form of a composite material applicable for water treatment (Pinto et al. 2004). The material for composite production as in the case of a polymer must be a blend of polymeric material that will be able to improve or modify the physico-chemical properties of the new polymeric composite material (Oprea 2008).

This method is a way of obtaining materials with the required engineering characteristics such as better chemical properties, biocompatibility, biological activities, thermal stability, open cell content, specific gravity and hydrophobicity properties. An improved way of enhancing the application of polymeric adsorbent material is to support the adsorbent materials in a template of porous matrices. This template can be used to support adsorbent material with desired characteristics for purification purposes, thus allowing for easier formulation cum production of blend filler with both physical and chemical characteristics closer to the desired adsorbent composite (Pinto et al. 2004, 2005; Oprea 2008).

In this study, polymeric composite adsorbent material (PCAD) was synthesised and characterised in our water research laboratory at the University of Johannesburg between April and October of 2013. The prepared composite material showed great affinity, high enrichment and less binding time with metal ions. The SPE extraction method was studied for Cd(II), Cr(III), and Pb(II) metal ions. The parameters that influence the sorption, extraction and elution efficiency of the metal ions were also studied.

Materials and methods

Reagents and standards

All reagents were analytical grade unless otherwise stated and Millipore water (Merck, Darmstadt, Germany) of 18 M Ω was used throughout the experiments. Concentrated nitric acid (HNO₃) (70 %) and hydrochloric acid (37 % HCl w/v) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All plastics and glassware were cleansed by soaking in dilute HNO₃ and were rinsed with distilled water prior to use. The metal-ion stock solution (1,000 mg/L) (Merck, Darmstadt, Germany) was prepared daily for obtaining reference and working solutions. The working standard solutions were prepared by mixing appropriate dilution of the stock standard solutions with distilled water. Ammonium acetate buffer solution (1 M) was prepared by mixing appropriate amounts of ammonia 25 % solution (Sigma-Aldrich St. Louis, MO, USA) and glacial acetic acid 97 % solution



(Sigma-Aldrich St. Louis, MO, USA), which was then followed by dilution with water to a final pH of 9.0 using Mettler Toledo pH meter model 20, Greifensee, Switzerland.

The working solutions were freshly prepared on a daily basis by the appropriate dilution of the stock with deionised water, while the calibration standards were prepared with serial dilutions of the stock mixture at 10, 20, 40, 60, 100, 200 and 500 ng/L. Hydrochloric acid HCl 0.1 M and sodium hydroxide NaOH 0.1 M solution were used to adjust the pH values of the working solutions. 1,2-dimethoxy-3-(1-methoxypropan-2-yloxy)propane (Sigma-Aldrich St Louis, MO, USA) was used as a triol, dibutyltin dilaurate (DBTL > 97 %, Merck, Darmstadt, Germany) was used as a catalyst, silicone oil and castor oil (Sigma-Aldrich St Louis, MO, USA) were used as a foam stabiliser. The isocyanates used were 4,4'-methylene diphenyl diisocyanate (MDI > 98 % Sigma-Aldrich St Louis, MO, USA) and 1,6-hexamethylene diisocyanate (HMDI > 98 % Lupanar, M 50, BASF Lemförde, Germany).

A StrataTM C18-E SPE C₁₈ (EC) cartridge (0.5 g, 6 mL, and polypropylene column) purchased from Phenomenex companies, Torrance CA, USA, was used for preconcentration. The porous frit was placed at the bottom and at the top of the column for allowing the adsorbent to settle. The SPE was carried out in a VasMaster-20 sample SPE station (Supelco, PA, USA). The SPE station was used for both sample loading and elution desorption flow rate.

Instruments

The analytes (metal ions) were determined using Spectro ARCOS inductively coupled plasma optical emission spectrometry ICP-OES with radial plasma equipped with Cetac ASX-520 auto-sampler (Borscht, Kleve, Germany). The operating conditions used for ICP-OES spectrometry during the measurements were as follows: RF generator forward power; 1,400 W, plasma argon flow rate 13 L/min, auxiliary argon flow rate 2.00 L/min, and nebuliser argon flow rate 0.95 L/min. The most prominent atomic and ionic analytical lines of metal ions selected for this experimental study were Cd 226.5 nm, Cr 205.55 nm, and Pb 220.35 nm. A cross-flow nebuliser and double-pass spray chamber were used throughout the measurement process. The calibration standards for ICP-OES analysis were prepared from high-purity compounds by diluting commercially available 1,000 mg/L solutions (Merck, Darmstadt, Germany) of varying elements in 1 % HNO₃.

Table 1 Composites of formulation of polyurethane composite adsorbent

| | Formulation series ^a | |
|--------------------------------------|---------------------------------|---------|
| | HMDI (A) | MDI (B) |
| Polyol (g) | 30 | 30 |
| DBTL (g) | 0.23 | 0.23 |
| Silicone oil: castor oil (1:1) (v/v) | 0.8 | 0.8 |
| Water content (%) | 3–5 | 1–5 |
| Diisocyanate (g) | 14.2 | 14.2 |
| Fillers (g) | 0.2 | 0.2 |

^a NCO index = 105 %, NCO = polyurethane bond (Pan et al. 2007; Pinto et al. 2004)

Polyurethane synthesis

The method of preparation was done according to Pinto et al. (2004) with slight modifications. A bulk total 50 g of the material, i.e. quantities required for the formation of a polyurethane composite such as polyol, distilled water, castor oil/silicone oil (1:1) and catalyst were added into a polyethylene flask and mixed vigorously for 1 min with a mechanical stirrer to obtain a formulated polyol prepolymer. The isocyanate was then added to the same flask followed by addition of the various fillers and stirred vigorously for about 20 min. The resulting mixture, a composite material was left undisturbed for about 60 s to allow the formulation to grow and form a PU polymer composite. The PU polymer composite was then immediately added into a mould and kept inside the oven at 60 °C for 60 min. The resulting formulation was thereafter ground to a powder and kept in desiccators until further analysis. Several formulations were tested for clarity but only one is reported here (Table 1). In order to maintain the urethane NCO index, isocyanate and water composition were varied (Table 1) for the series formulation.

Solid-phase extraction (SPE) cartridge

The SPE commercial cartridge was replaced with polyurethane composites adsorbent (PCAD) (polymeric material containing polyurethane, AC and β-CD as filler) packed cartridge, which was prepared by modifying a StrataTM C18-E SPE C₁₈ (EC) cartridge (0.5 g, 6 mL polypropylene). The C₁₈ packing of the cartridge was evacuated, and then 0.5 g of PCAD was packed into the cartridge. The 20 μm polypropylene lower and upper frits remained at each end of the cartridge to serve as support holders for PCAD packing. The outlet tip of the



cartridge was connected to a vacuum pump (Shimadzu, Japan) and the inlet end of the cartridge was connected to PTFE suction tube whose other end was inserted into sample solution. The entire SPE set-up assembly was carefully washed with methanol before use in order to reduce the interferences of the organic and inorganic contaminants.

Procedure

Before the preconcentration enrichment step, the PCAD packed cartridge was firstly preconditioned by washing using triple distilled water followed by conditioning with 10 mL of ammonium acetate buffer (1.0 M, pH 9.0). The sample solutions were then loaded onto the preconditioned PCAD cartridge at a constant flow rate. After the loading stage, the PCAD packed cartridge was then washed with 5 mL ammonium acetate buffer. The washing stage before metal-ion desorption was engaged in order to eliminate concomitant elements that could be partially adsorbed by the PCAD polymeric material. The retained metal ions were then eluted with nitric acid at a constant flow rate into ICP vials. The metal concentrations in the final solutions were then determined by ICP-OES. The same protocol was employed for the blank solutions. After each run, the PCAD polymeric material in the cartridge was washed with 20 mL of distilled water and then stored for further experiments. The pH of samples was adjusted accordingly with 1 mL of 0.1 M HCl or 0.1 M NaOH solution. Thereafter a known volume of sample solutions were aspirated through the modified SPE C18 column at a controlled flow rate and the eluate obtained was discarded. However, when the whole sample had passed through the SPE column, 10 mL of purified water was used to remove the impurities or the co-adsorbed matrix materials from the cartridge. The influence of sample solution pH, sample volume, sample loading flow rate, elution flow rate, type and concentration of eluents were investigated.

Results and discussion

Characterisation of the polyurethane composite adsorbents

The structure and surface functional groups on the PCAD with different fillers was investigated and compared by using Fourier transform infrared (FT-IR) and scanning electron microscopy (SEM) for their characterisation.

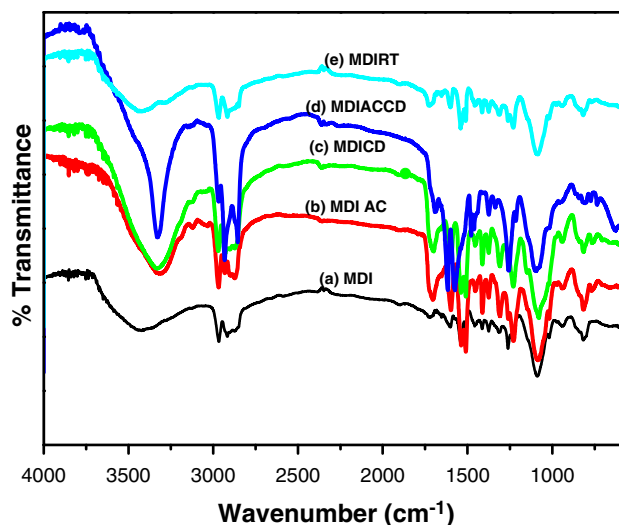


Fig. 1 FT-IR transmission spectra of PCAD spectra of (a) MDI; (b) MDIAC; (c) MDICD; (d) MDIACCD; and (e) MDIRT

FT-IR spectroscopy

The surface functional groups on the PCAD material were investigated using FT-IR spectroscopy (Nicolet IS10 SMART ITR, Madison, WI, USA) equipped with Golden Gate single reflection attenuated total reflection (ATR) accessory. All the polymeric materials, i.e. methylene diisocyanate (MDI), methylene diisocyanate-activated carbon (MDIAC), methylene diisocyanate- β cyclodextrin (β -CD) (MDICD), methylene diisocyanate-activated carbon- β cyclodextrin (MDIACCD), and methylene diisocyanate raw tassel (MDIRT) were prepared onto FT-IR grade KBr crystals at a sample-to-crystal ratio of 20:80. Figure 1 shows the FT-IR spectra of the polymeric materials.

The typical FT-IR spectra of the polymeric material PCAD for the composite adsorbent are shown in Fig. 1. All the characteristic absorption peaks of PCAD polymeric materials, around 3,430–3,300 cm^{-1} (free O–H stretching vibration, N–H stretching of hydrogen bonded amino group), 2,970–2,840 cm^{-1} (CH_2 and CH_3 stretching vibration), 1,720–1,600 cm^{-1} ($\text{C}=\text{O}$ stretching of bonded carbonyl), 1,400–1,305 cm^{-1} ($\text{C}-\text{N}$) and 1,100–1,000 cm^{-1} ($-\text{C}-\text{O}-\text{C}$) revealed the existence of the urethane in the synthesised cross-linked PCAD and fillers in the polymeric materials. The absorption of NCO from the PCAD polymeric materials takes place between 2,300 and 2,200 cm^{-1} in different spectra for MDI-based PCAD polymeric materials which was not observed in any of the resulting polymeric materials, thus indicating the absence of free NCO groups. All the peaks at 3,430–3,300 cm^{-1} were very broad for the PCAD except



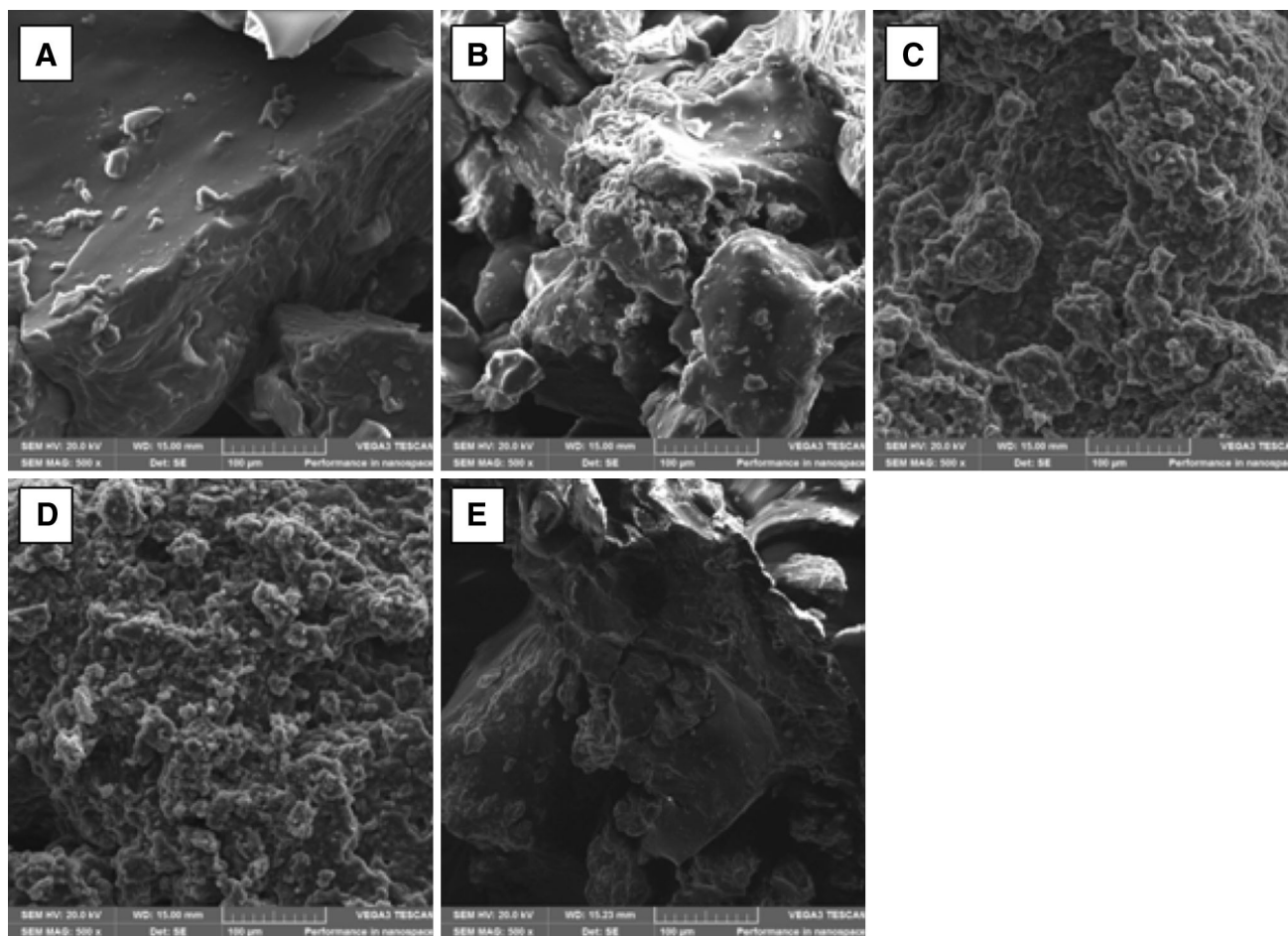


Fig. 2 Scanning electron microscope (SEM) images of PCAD polymeric material at $\times 500$ nm: **a** MDI; **b** MDIAC; **c** MDICD; **d** MDIACCD; **e** MDIRT

for MDIACCD that has a sharp peak at this region. These peaks were shifted to higher absorption band than $3,300\text{ cm}^{-1}$ when compared to the broad absorption of OH stretching vibration in the range of $3,500\text{--}3,300\text{ cm}^{-1}$. This might be due to the OH stretching vibration from β -CD (Pinto et al. 2004; Oprea 2011).

However, with the introduction of more filler into the PU matrix, in the PCAD polymeric material, the peak at $1,095\text{ cm}^{-1}$ for MDIACCD shifts to $1,018\text{ cm}^{-1}$ for MDI (Fig. 1). Similar observations were noticed at peak 784 cm^{-1} for MDIAC which shifted to 773 cm^{-1} for MDIACCD and was completely absent in both MDI and MDIRT. This peak shift is attributed to out-of-plane vibration of the CO–NH group. The stretching vibration observed for MDI and MDICD at 940 cm^{-1} is due to the C–O bond stretching vibration. The C–O bond stretching vibrations observed at $818\text{--}816\text{ cm}^{-1}$ in MDI, MDICD,

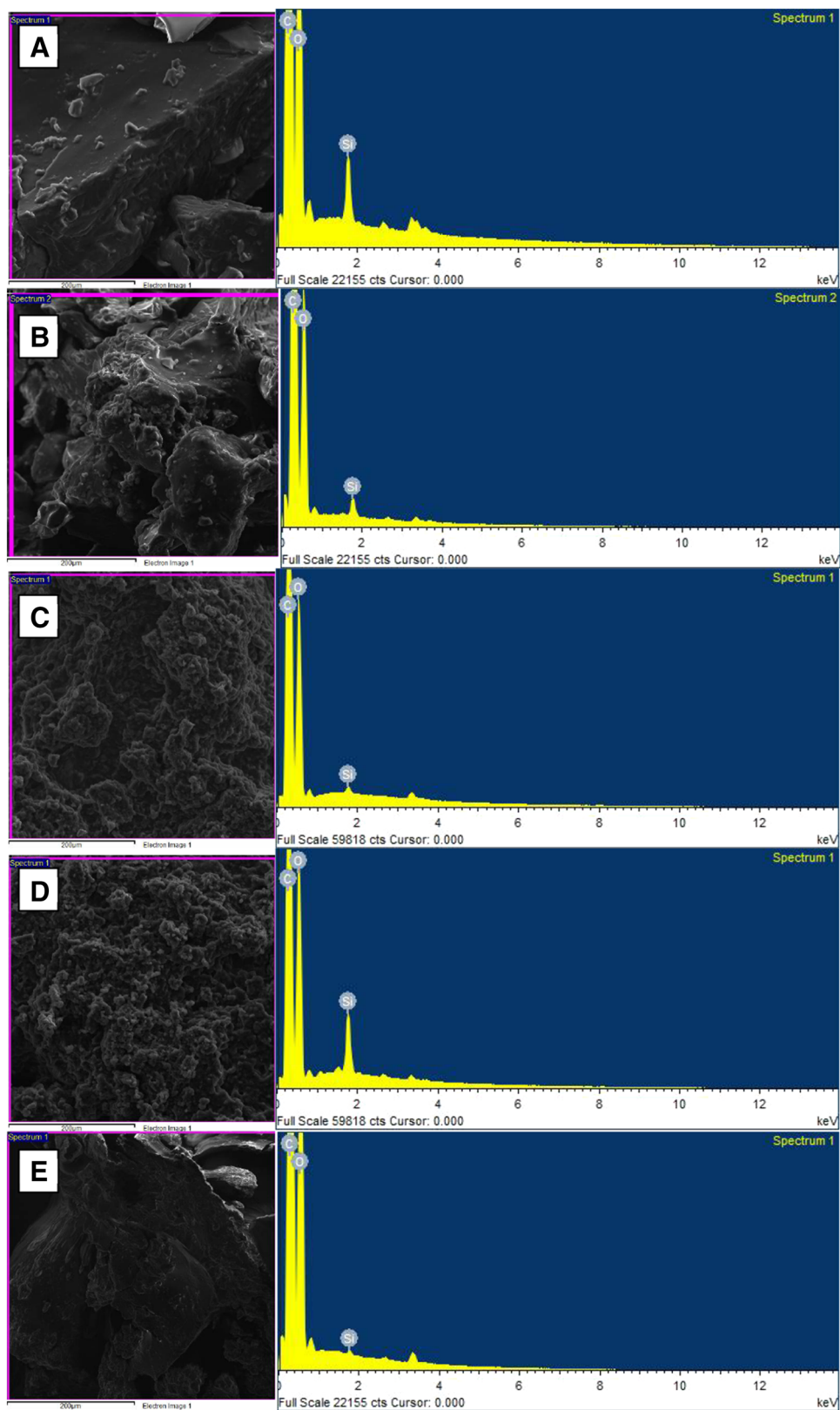
and MDIRT were due to anhydroglucose ring stretching vibration (Pinto et al. 2004; Oprea 2011). The hydroxyl (–OH) groups and the –O– groups from the filler, especially β -CD and AC, form H bonds with C=O groups and N–H groups from the polymeric PCAD material. This formation, i.e. hydrogen bond formation between the PU macromolecules and the fillers, results in the increase of physical cross-links in the PCAD polymeric composite materials (Pinto et al. 2004; Oprea 2011).

Surface morphology of PCAD using SEM

The surface morphology of PCAD polymeric material was observed by scanning electron microscope (SEM) (TESCAN VEGA 3 LM, Czech). The representative SEM images (Fig. 2) reveal the microstructure transformation on the surface of the polymeric material. All the PCAD polymeric material shows different surface morphology.



Fig. 3 SEM and EDX images of PCAD polymeric material at $\times 500$ nm: **a** MDI; **b** MDIAC; **c** MDICD; **d** MDIACCD; **e** MDIRT



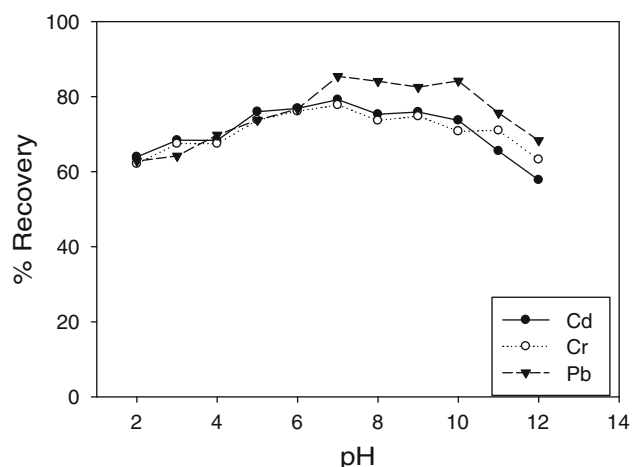


Fig. 4 Influence of solution pH values on the recoveries of metal ions in aqueous medium

The results show that the filler contributes significantly to the final texture of the polyurethane composite material PCAD. The addition of the filler, indicated in Fig. 2a (MDI) to Fig. 2e (MDIRT), shows that the soft segment part of the urethane chain NCO plays a predominant role, compared to the hard segment, especially in Fig. 2b–d. As can be seen in Fig. 2d the MDIACCD containing β -CD and AC is shown to be more porous than the remaining PCAD polymeric material. This might be due to the effect of β -CD which has inclusion properties and can incorporate AC as a guest into its moiety. The result for Fig. 2e (MDIRT) shows that the raw tassel RT is acting as a binder to reinforce the hard segment part of the PU chain, hence the flatter and smoother surface. The MDI surface (Fig. 2a) is smoother than the other because of the absence of the filler in the polymeric material.

Surface morphology of PCAD using SEM coupled with energy dispersive X-ray (EDX)

The provided sample was anchored onto the sample holder and inserted into TESCAN VEGA 3 LM SEM integrated fully with a selected EDX microanalysis which was an oxford system. The working voltage of 20 kV was used to analyse the composite material. Approximately 70 % of the study area was scanned for particles, avoiding the edges for unwanted particles due to handling. Figure 3a–e shows the residue observed on the composite material. Particles containing high signal of carbon (C), oxygen (O), and silicon (Si) was from the starting material which contain silicone oil and polyurethane linker diisocyanate. Particles containing traces of sodium (Na), together with potassium (K), chlorine (Cl), cobalt (Co), and Calcium (Ca) were

probably from organic dust in sample chamber (result were not reflected on the EDX graph). The high percentage of C in all the samples was due to the starting material (Table 1) and carbon tape used to collect the particles therefore, C signal in each of the spectra was partially associated with the tape. While O and Si were from also from the starting material.

Influence of solution pH

The pH of aqueous solution sample plays major role for quantitative retention of analytes because of the competitive reactions nature, between metal ions and hydrogen ions in aqueous solution (Zhang et al. 2010). Furthermore, pH influences both the chemistry of metal ions and functional groups on polymeric material due to its metal-retention ability from aqueous solution which is a pH-dependent process (Baraka et al. 2007).

The influence of pH on the retention of analytes [Cd(II), Cr(III) and Pb(II) ions] onto the polymeric material was investigated in the pH range of 4.0–10.0. The sample solutions of each metal ion were investigated by varying the pH of metal solutions subjected to extraction experiments by using dilute sodium hydroxide or dilute nitric acid solution. The experiment was carried out using 100 mL of 4 ng/L for Cd, 20 ng/L for Cr and 80 ng/L for Pb which were passed through the PCAD packed cartridge.

The retained metal ions on the PCAD polymeric material were stripped from the column using nitric acid. The percentage recovery as a function of pH for all the metal ions is shown in Fig. 4. The plots (Fig. 4) reveal that the PCAD polymeric material can be applied easily in extraction experiments in acidic-neutral medium, because it showed more than 70 % average recovery for all the metal ions in the pH range of 5.0–8.0 and having the maximum recovery at pH 7. At a pH value of above 5, the main group responsible for metal extraction, carboxylic acids (El-Sayed et al. 2010; Castro et al. 2011), is protonated due to the high concentration of H^+ species. The result also reveals that as the pH of sample solution increases the concentration of the metal ions also decreases. The recoveries were slightly lower at lower pH values. This could be due to the competition between the metal ion and hydrogen ion/hydronium ions species for active sites which is responsible for metal-ion retention (El-Sayed et al. 2010). Thus, the increase in recoveries with increasing pH (Fig. 4) could be due to a decrease in positive charge density on the PCAD polymeric material. Thus, the reduction of positive charge density will result in the enhancement of metal-ion retention (Gode and Moral 2008).



The influence of eluent flow rate

The influence of the eluent flow rate is one of the vital parameters affecting preconcentration and recovery percentage of the metal ions. It was observed from the results obtained as shown in Fig. 5, that the recoveries of the metal ions changed between 64 and 82 % for sample flow rates of between 1 and 2 mL/min and between 65 and 87 % for sample flow rates of between 3 and 5 mL/min. Thus, the recoveries of metal ions for the various elution (desorption) flow rates were found to be between 64 and 86 %. The variation of the elution flow rate was minimal with not much significant effect. The flow rate of

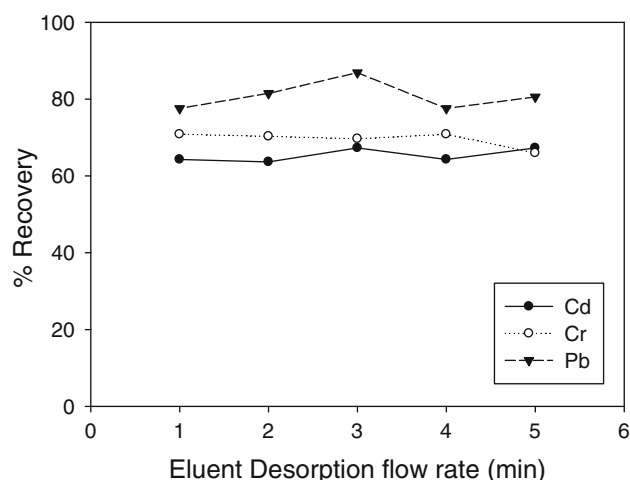


Fig. 5 Influence of desorption flow rate on the recoveries of metal ions in aqueous medium

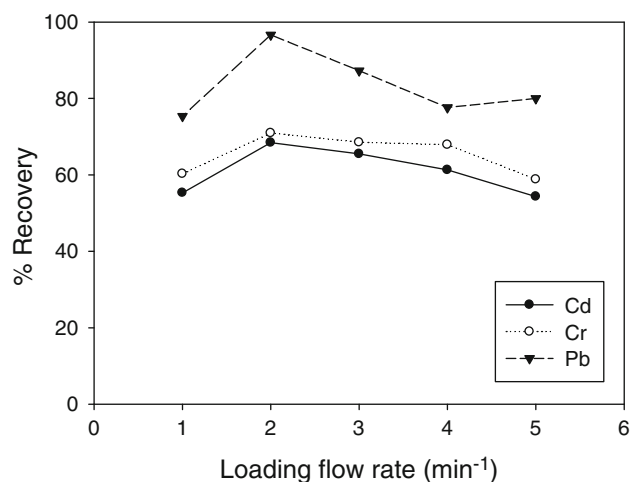


Fig. 6 Influence of sample loading flow rate on the recoveries of metal-ion mixtures in aqueous medium

3 mL/min was selected as the optimum flow rate for the desorption elution and was subsequently used for other experimental test runs.

Influence of sample loading flow rate

The sample loading flow rate is one of the most important parameters in obtaining both the quantitative retention and elution of the analytes, respectively (Sharma and Pant 2009; Sabermahani et al. 2011). The influence of sample loading flow rates on retention of metal ions was investigated in the flow rates ranging between 1 and 5 mL/min. The result (Fig. 6) shows that at a flow rate of between 1 and 2 mL/min, there was a sharp increase in the recovery of metal ions. At the flow rates greater than 3 mL/min, there was a decrease in metal-ion recovery. This could be due to the speed at which the sample solution passes through the cartridge column. Thus, the timing is not adequate for the equilibrium to be established between the surface of the adsorbent and the analytes which eventually leads to a reduction in analyte recovery (Sharma and Pant 2009; Sabermahani et al. 2011). Thus, a flow rate of 2 mL/min was selected for subsequent experimental test runs.

Influence of the type and concentration of eluents

The quantitative recovery of retained metal ions on PCAD polymeric materials, various concentration and volumes of nitric and hydrochloric acids were investigated. The influence of eluents type on the recovery of metal ions was also studied using nitric acid. The results given in Fig. 7 show that the quantitative recoveries (80 %) for the metal ions were obtained with 50 mL of 2 mol/L of HNO₃. Thus, in this study 20 mL of 2 M HNO₃ was selected as eluents for the metal recovery.

The effect of different concentrations of nitric and hydrochloric acids on the preconcentration yields of the metal ions under the optimum pH condition was studied. The result shows that both acids can effectively elute the metal ions from PCAD polymeric materials in the cartridge (Fig. 7). However, HNO₃ has higher recoveries than HCl and one would expect both acids to have the same recovery capacities as shown in Fig. 7. However, this is not the case, despite both acids having the same hydroxonium ion. HNO₃ has an edge due to its oxidation capacity (Malla et al. 2002). It was also observed that HCl has a low recovery at 3.0 M as shown in Fig. 7. This could be due to the formation of stable complexes in the presence of chloride ions which



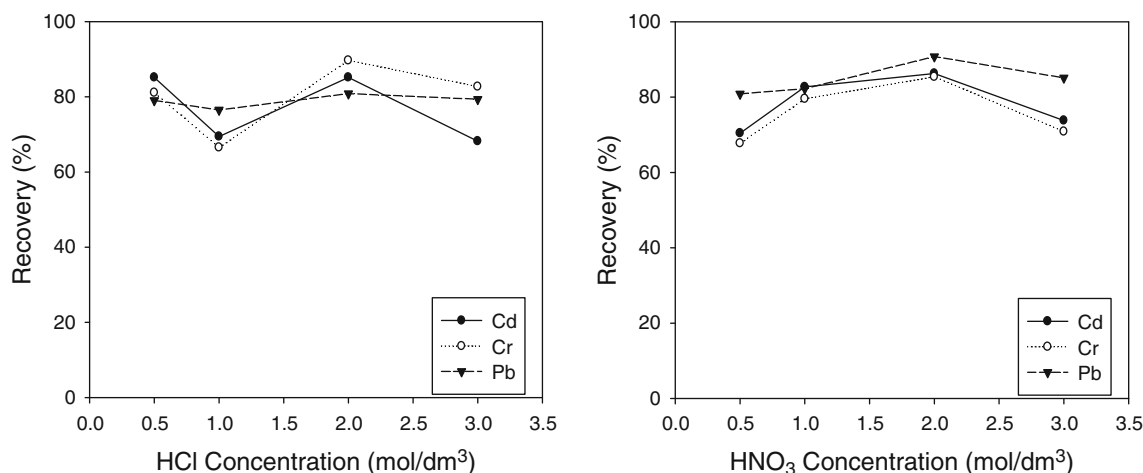


Fig. 7 Influence of type and concentration of eluents on the recoveries of metal ions in aqueous medium

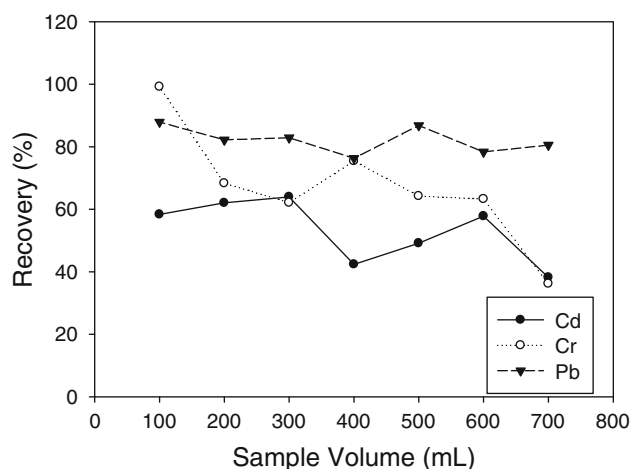


Fig. 8 Influence of sample volume on the recoveries of metal ions in aqueous medium

explain the low recovery experienced for HCl when used as eluents (Tuzen et al. 2005). Thus, HNO₃ was selected as eluents for desorption of the metal ions from PCAD polymeric material.

Influence of sample volume

The influence of the sample volume on the recovery and preconcentration factor is one of the vital parameters for obtaining high exchange capacity (Ngah et al. 2012). In order to determine the maximum applicable sample volume for analyte concentration, there is a need to examine the possibility of enriching low concentrations of analytes from large sample volumes. To achieve this purpose, the

concentrations of each metal ion were kept relatively constant with increasing sample volume. The influence of sample volume was studied by passing 100–500 mL of model sample solution through PCA polymeric materials packed cartridge under the optimum conditions (Fig. 8). The recoveries of the metal-ion analytes were greater than 70 %. The preconcentration factor was calculated by the ratio of highest volume to the lowest volume of eluents. Hence, 5 mL sample volume solution was adopted for the preconcentration factor.

Comparison of PCAD polymeric material with other methods of metal-ion extraction

The comparison of PCAD polymeric material with other methods of extraction was carried out to show the extraction efficiency and determination of metal ion in water sample. The comparison result (Fig. 9) showed that PCAD polymeric materials were applied as a stationary phase to preconcentrate and purify metal ions in aqueous solution. The average recoveries of PCB analytes for all PCA polymeric material including AC and C18 (59 % for MDI, 82 % for MDIAC, 85 % for MDICD, 92 % for MDIACCD, 65 % for MDIRT, 70 % for AC and 76 % for C18 cartridge) revealed that the PU composite material with the filler β -CD and AC, i.e. MDIACCD (Fig. 9) enhances the extraction efficiency of PCBs more than the other extraction techniques.

Method validation

A series of standard solutions were prepared to obtain a linear range for each of the metal-ion analytes. Table 2



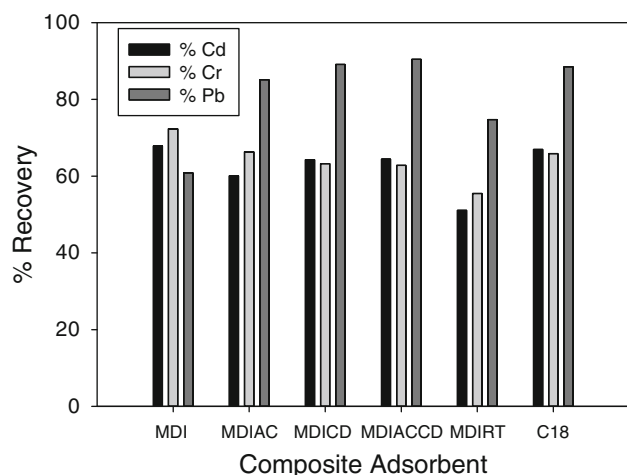


Fig. 9 Influence of composite adsorbents on the recoveries of metal ions in aqueous medium

Table 2 The limit of detection, limit of quantification and reproducibility method

| Analytes | Calibration equations | Linear correlation coefficients (r^2) | LOD (ng/mL) | LOQ (ng/mL) |
|------------------|-----------------------|---|-------------|-------------|
| Cd ²⁺ | $Y = 0.269x + 1.731$ | 0.936 | 0.256 | 0.855 |
| Cr ³⁺ | $Y = 0.186x + 11.15$ | 0.988 | 0.249 | 0.831 |
| Pb ²⁺ | $Y = 0.276x + 1.555$ | 0.963 | 0.252 | 0.841 |

shows the linearity range of the prepared standard solutions. The correlation coefficient (r^2) of the PCB analytes ranges between 0.936 and 0.988. The limit of detection LOD which is a signal-to-noise ratio (3:1) or response of standard deviation to the slope of analytical curve ($3.3 \times \frac{s}{b}$) ranges from 0.249 to 0.256. The limit of quantification (LOQs) based upon the signal-to-noise ratio (10:1) or standard deviation of the blank on the residual regression line ($10 \times \frac{s}{b}$) ranges between 0.831 and 0.855 of the metal-ion analytes. A comparison of the method and adsorbent material is shown in Fig. 9. The obtained LOD and LOQ are comparable with some reported studies (Ensafi et al. 2003; Otero-Romani et al. 2005; Huang et al. 2008; Sharma and Pant 2009).

Conclusion

The present study demonstrates the preparation and use of an adsorbent based on polyurethane synthesis with different kinds of fillers. The modification of the polymeric composite material is simple and the composite material

produced remained firm and could easily be packed into the SPE cartridges which invariably allowed it to be used several times. It could be concluded from the results that the PCAD produced is an effective adsorbent for preconcentration of metal ions from various sample solutions. The merit of the composite material includes high enrichment factor of (90), reproducibility, and low cost. The reusability of the adsorbent is high; about ten cycles without any loss in its adsorption capability.

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