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Development of magnetic porous coordination polymer adsorbent for the removal and preconcentration of Pb(II) from environmental water samples

Aisha Mohammed Al’Abri1,2, Sharifah Mohamad1,3, Siti Nadiah Abdul Halim1, Nor Kartini Abu Bakar1

Abstract
A novel porous coordination polymer adsorbent (BTCA-P-Cu-CP) based on a piperazine(P) as a ligand and 1,2,4,5-benzenetetracarboxylic acid (BTCA) as a linker was synthesized and magnetized to form magnetic porous coordination polymer (BTCA-P-Cu-MCP). Fourier transform infrared (FTIR), X-ray diffraction (XRD), vibrating sample magnetometer (VSM), field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDS), CHN, and Brunauer–Emmett–Teller (BET) analysis were used to characterize the synthesized adsorbent. BTCA-P-Cu-MCP was used for removal and preconcentration of Pb(II) ions from environmental water samples prior to flame atomic absorption spectrometry (FAAS) analysis. The maximum adsorption capacity of BTCA-P-Cu-MCP was 582 mg g⁻¹. Adsorption isotherm, kinetic, and thermodynamic parameters were investigated for Pb(II) ions adsorption. Magnetic solid phase extraction (MSPE) method was used for preconcentration of Pb(II) ions and the parameters influencing the preconcentration process have been examined. The linearity range of proposed method was 0.1–100 μg L⁻¹ with a preconcentration factor of 100. The limits of detection and limits of quantification for lead were 0.03 μg L⁻¹ and 0.11 μg L⁻¹, respectively. The recoveries from 94.75 ± 4 to 100.93 ± 1.9% were obtained for rapid extraction of trace levels of Pb(II) ions in different water samples. The results showed that the BTCA-P-Cu-MCP was steady and effective adsorbent for the decontamination and preconcentration of lead ions from the aqueous environment.

Keywords Magnetic coordination polymer · Magnetic solid phase extraction · Lead · Adsorption

Introduction
Globally, environmental pollution caused by heavy metals has received extensive attention due to their toxicity, bioaccumulation as well as long persistence (Anantha and Kota 2016; Bárcena et al. 2017; Rajeshkumar et al. 2018). Lead ions (Pb²⁺) has been recognized as one of the most toxic forms of heavy metals and classified as the second hazardous heavy metal among 129 pollutants according to the U.S Environmental Protection Agency (EPA). It significantly harmfully affect human health and the environment even at trace level (Chao et al. 2014; Dahaghin et al. 2017; He et al. 2017; Luo et al. 2016; Shahat et al. 2018; Wang et al. 2015; Yin et al. 2016). Major lead release sources are sulfide ore smelting, fossil fuel combustion, mining, agriculture, battery manufacturing, and paper and pulp industries (Lu et al. 2015; Rajput et al. 2016). Lead can cause many health diseases such as brain, nervous, skeletal, circulatory, enzymatic, endocrine, reproductive, and immune systems damage as well as anemia, kidney malfunctioning, and gastrointestinal tract alterations. Indeed, lead poisoning as low as 10 ppb mainly affected children by decreasing intelligence and slowing neurological development (Chao et al. 2014; Jellali et al. 2016; Salarian et al. 2014; Wang et al. 2013). Afterward, there is a crucial need to...
develop novel methods for the removal of trace lead. To date, several methods have been reported for efficient heavy metals removal from wastewater. These include membrane separation, chemical precipitation, coagulation, sedimentation, reverse osmosis, and adsorption. Among these methods, adsorption has been shown to be an economical alternative for removing trace metals from water (Afkhami and Norooz-Asl 2009; Chen et al. 2015; Luzardo et al. 2017; Yin et al. 2016; Zahri et al. 2017).

Since the presence of Pb(II) ions in trace level as well as the influence of matrix ions in analyzed samples, the direct determination in real samples is a challenging task (Mashkani et al. 2018). Consequently, in order to enhance sensitivity and effectively remove matrix interferences from the samples, the pre-treatment methods former to instrumental analysis are necessary (Tokalıoglu et al. 2017). To date, in various publications, different extraction methods have been reported such as liquid–liquid extraction (LLE), cloud point extraction, ion exchange precipitation/co-precipitation, and solid phase extraction (SPE) (Hassanpour et al. 2015; La Colla et al. 2015; Farajzadeh et al. 2014; Yilmaz et al. 2015). Nevertheless, solid phase extraction (SPE) is the superior technique used in preconcentrating of trace levels of Pb(II) ions in water samples due to its simplicity, high enrichment factor, ability to eliminate matrix interferences, fast extraction, consumption of low volume of organic solvent, and environment friendly (Baghban et al. 2017; Faraji et al. 2016; Khan et al. 2016; Mashkani et al. 2018; Tokalıoglu et al. 2017; Taheri et al. 2014; Yilmaz et al. 2015). Since solid phase extractor plays a key role in SPE, development of new sorbents for SPE has taken a great interest of recent studies (Mashkani et al. 2018; Tokalıoglu et al. 2017; Tuzen et al. 2016). Chelating polymeric resins, carbon nanotubes, nanoporous silica, metal organic frameworks, and different bio-sorbents have been used to adsorb heavy metals (Abdefiattah et al. 2016; Liu et al. 2016; Mahmoud et al. 2016).

In recent years, combining SPE with magnetic separation, so-called magnetic solid phase extraction (MSPE), has attracted more interest and attention due to its simplicity, low cost, time-saving, and economic as well as improving the separation and preconcentrating process. In MSPE, the magnetic adsorbent with the captured analytes can be separated from the matrix via an external magnetic field (Farajzadeh and Mohebbi 2018; Fayazi et al. 2016; Naeimi and Faghihian 2017a). Fe3O4 nanoparticles are perfect magnetic nanoparticles that have been used in MSPE due to their small size, inexpensive, superparamagnetic, and low toxicity, as well as leads to chemical stability and reusability of the adsorbents (Kakavandi et al. 2013; Liang et al. 2018; Naeimi and Faghihian 2017a; Setiadi et al. 2017).

Recently, coordination polymer (CP) is one of the most promising types of materials that attracted a lot of research interests. CPs are crystalline materials consisting of metal ions and organic linker connected by strong coordination bonds. CPs have shown high potential in gas storage, drug delivery, catalysis, and chemical sensing and separation due to their unique properties such as extensive porosities, surface properties, and tunable pore shapes and sizes (Calvin et al. 2018; Carrington et al. 2017; Luo et al. 2017; Seoane et al. 2016). A combination of CPs with magnetic nanoparticles (MNPs) leads to extraordinary interest because the new composite possesses the advantages of both MNPs and CPs. As reported, the stability and reusability of CPs in aqueous solution can be significantly enhanced by MNPs modification (Shi et al. 2018).

In previous studies, Babazadeh et al. used \([\text{Fe}_3\text{O}_4–\text{ethylene diamine}]/\text{MIL-101(Fe)}\) to preconcentrate Cd(II), Pb(II), Zn(II), and Cr(III) in different matrices (Babazadeh et al. 2015). Also, Tadjarodi et.al and Dahaghin et.al used magnetized HKUST-1 (MOF-199) and Fe3O4@SiO2@IP respectively for extraction of Pb(II) from different real samples (Dahaghin et al. 2017; Ghorbani-Khalhor 2016). In these studies, the results showed that these methods are sensitive for lead extraction, since the limit of detection was 0.48–0.80 μg L−1 which is lower than the standard permissible limit of lead in drinking water (10 μg L−1) according to the WHO (Bhattacharjee et al. 2003; Nath et al. 2018; Ponsadailakshmi et al. 2018) specification. However, the sorption time and elution time for Pb2+ extraction were 10–15 and 7–15.2 min as well as the sorption capacity was 105–198 mg g−1. These parameters are very critical in analytical chemistry. Therefore, development of a sorbent which can shorten the time analysis and has high sorption capacity is very important task.

Herein, a novel porous coordination polymer (BTCA-P-Cu-CP) was synthesized in a room temperature using 1,2,4,5-benzetetracarboxylic acid (BTCA) and piperazine (P) coordinated with cupper metal ions. Tetracarboxylate groups in BTCA can bind through hydrogen bonding interactions in different direction resulting in formation of extended structures. In addition, N atom in piperazine provide more bonding sites for heavy metals via additive bonding as reported (Shi et al. 2018). Consequently, the different bonding modes resulting in high porosity of the new composite potentially provide adequate surface for adsorption process.

The recently synthesized BTCA-P-Cu-CP was magnetized with Fe3O4 (MNPs) and the prepared composite (BTCA-P-Cu-MCP) has magnetic characteristics and high porous properties. The adsorption properties of the BTCA-P-Cu-MCP were studied by adsorption of Pb(II) ions in aqueous solutions and the total concentration of Pb(II) ions in extracted phase was then determined by FAAS. Furthermore, BTCA-P-Cu-MCP adsorbent was successfully used in MSPE method for preconcentration of Pb(II) ions from water samples. The proposed MSPE provided excellent analytical performances, i.e., wide dynamic range, high preconcentration factor, high
selectivity, good repeatability, and reproducibility. The LOD obtained is 333 times lower than the WHO standard permissible limit of lead in drinking water (10 μg L−1). Furthermore, the results showed the applicability of BTCA-P-Cu-MCP sorbent for simple and fast extraction of Pb(II) ions which may open a new perspective in the treatment of lead water pollution.

Experimental section

Materials and reagents

All the reagent and chemicals were of analytical reagent grade and used as received. CuCl2.2H2O (98%), N, N-dimethyl formamide (99.8%), thiourea (98%), ethylenediaminetetraacetic acid (99.5%), acetic acid (99.8%), ammonium hydroxide (30%), methanol (99.8%), and ethanol (95%) were obtained from R&M chemicals (Essex, UK), while hydrochloric acid (37%), nitric acid (65%), sulfuric acid (97%), and lead (II) nitrate were purchased from Merck chemicals (Darmstadt, Germany). Piperazine (99%), benzene-1,2,4,5 tetracarboxylic acid (96%), FeCl2.4H2O, FeCl3.6H2O, (99%), and NaCl (99.5%) were brought from Sigma-Aldrich (China).

Stock solution of 100 ppm was prepared by dissolving 0.01598 g of pure lead nitrate in 1% (v/v) nitric acid solution in a 100-ml volumetric flask and stored in a refrigerator at 4 °C. Working standard solutions were prepared by diluting the stock standard solution to the required concentrations. Three real environmental water samples were analyzed in this work. The tap water was obtained from our laboratory, river water from Kuala Langat, Selangor, and well water from Nizwa, Sultanate of Oman.

Instruments

FTIR spectrometry (Spectrum 400 PerkinElmer-USA) was done using the ATR technique in absorption mode with eight scans and a wavenumber range of 4000 to 450 cm−1 with a diamond detector. Powder X-ray diffraction (PXRD) studies were carried out on a PAN analytical EMPYREAN with monochromator Cu Kα radiation (λ = 15.41874 Å) in the 2θ range of 5 to 40° with a slit size = 0.4785. Morphological analysis of the synthesized products was performed using a JEOL JSM-7600F field emission scanning electron microscope operated at 3 kV (JEOL, Tokyo Japan). Elemental analyses were performed using CHN analyzer LECO model CHNS-932 and Perkin Elmer CHNS/O Analyzer series II 2400 (Waltham, MA, USA). Brunauer–Emmett–Teller (BET) analysis was performed using a Micromeritics ASAP2020 surface area analyzer for measuring the surface area, pore volume, and pore size of the products (Micromeritics, Georgia, USA). The magnetic properties were analyzed by using vibrating sample magnetometer (VSM LakeShore 7400 series, Tokyo, Japan). A flame atomic absorption spectrometer (FAAS) Perkin Elmer Analyst 400 (Uerlingen, Germany) equipped with an electrodeless discharge lamp (EDL) for lead was used in the analyses. The FAAS was operated with acetylene and airflow rates of 2.05 L min−1 and 10.0 L min−1 respectively. For determination of Pb(II) ions, 283.3 nm wavelength, 5.0 mA lamp current, and 0.5 nm slit width were utilized.

Synthesis method

Synthesis of BTCA-P-Cu-CP

BTCA-P-Cu-CP was synthesized via room temperature method as in literature with some modification (Sherino et al. 2018). A mixture of CuCl2.2H2O (5 mmol) and piperazine (2.5 mmol) was stirred for 10 min at room temperature; blue precipitate was obtained. Then, benzene-1,2,4,5 tetracarboxylic acid (1.25 mmol) was added to the reaction mixture and stirred for 4 h (400 rpm) at ambient temperature. The resulting product was centrifuged and washed with ethanol and DI water. Finally, the product, BTCA-P-Cu-CP, was dried in a vacuum oven at 70 °C.

Magnetization of BTCA-P-Cu-CP

MNPs were prepared by a co-precipitation method according to the previously reported method (Kiasat and Nazari 2013). BTCA-P-Cu-MCP nanocomposite was synthesized as in reported methods with some modifications (Bagheri et al. 2012; Ke et al. 2011). An aqueous solution of CuCl2.2H2O (5 mmol, 40 ml DI water) and piperazine (2.5 mmol, 40 ml DI water) were mixed under magnetic stirring for 10 min at ambient temperature. Benzene-1,2,4,5 tetracarboxylic acid (1.25 mmol) was dissolved in a mixed solution of DMF/ethanol (1:1, 80 mL) followed by the addition of 37 mg of dispersing MNPs in 10 mL ethanol and stirred at 70 °C for 10 min. Then, the two reaction mixtures were added and stirred for further 4 h at 70 °C. The resulting products were collected by centrifugation and washed three times with DI water and two times with ethanol. Finally, the greenish BTCA-P-Cu-MCP was dried in oven at 70 °C.

Adsorption of Pb(II) ions

Adsorption process was carried out for Pb(II) in water sample. Batch adsorption procedures were used to optimize the effect of pH, adsorbent dosage, and contact time. Experiment was carried out as following the steps: specific amount of the adsorbent was added to 10 mL of water sample spiked with specific concentration of Pb(II) ions followed by shaking
(using an Orbital shaker). Then, the adsorbent was collected using an external magnet and the residual concentration was determined using FAAS. For the thermodynamic study, the experiment was carried out at different temperatures while for the isotherm study, the experiment was done at room temperature with different initial Pb(II) ions concentration. The removal efficiency, \( R(\%) \) was calculated by using Eq. (1).

\[
R(\%) = \frac{(C_i - C_e)}{C_i} \times 100
\]  

Eq. (1)

The equilibrium adsorption capacity \( q_e (\text{mg g}^{-1}) \) of the synthesized was calculated using Eq. (2)

\[
q_e = \left( \frac{V}{m} \right)(C_i - C_e)
\]  

Eq. (2)

and the adsorption capacity \( q_t (\text{mg g}^{-1}) \) at time \( t \) was obtained from Eq. (3)

\[
q_t = \left( \frac{V}{m} \right) (C_i - C_e)
\]  

Eq. (3)

where \( m \) is the mass of adsorbent (mg), \( V \) is the initial sample volume (mL), \( C_i \) and \( C_e \) are initial concentration and residual concentration after equilibrium of Pb(II) ions (mg g\(^{-1}\)) respectively, and \( C_i \) (mg g\(^{-1}\)) is the concentration of Pb(II) ions at time \( t \).

**Preconcentration of Pb(II) ions**

Magnetic solid phase extraction method was used to develop the preconcentration of Pb(II) ions and described as follows:

3 mg of adsorbent was mixed with 10 ml of Pb(II) ions known as concentration and shaken (250 rpm) for 5 min. Then, the adsorbent was separated by magnetic decantation and appropriate volume of elution solvent was added and then the mixture was sonicated for suitable time. Finally, after the adsorbent was gathered by using an external magnet, the solution was filtered using a PTFE syringe filter (13 mm, 0.22 mm pore size) and introduced to FAAS to determine the concentration of Pb(II) ions as illustrated in Fig. 1. The percent extraction of lead, was calculated by using the following equation:

\[
\text{Extraction recovery } \% = \frac{C_e}{C_i} \times 100
\]  

Eq. (4)

where \( C_i \) is the concentration of Pb(II) ions (mg L\(^{-1}\)) in the solution before extraction and \( C_e \) is the extracted Pb(II) ions (mg L\(^{-1}\)).

**Reusability of the adsorbent**

To evaluate the stability and reusability of the used BTCA-P-Cu-MCP, the regeneration of Pb-loaded BTCA-P-Cu-MCP was performed in five repeated cycles. Ten milliliters of Pb(II) ions (10 ppm) was shaking for 5 min with specific mass of BTCA-P-Cu-MCP. The magnetic sorbent with adsorbed Pb(II) ions was separated from the mixture using a permanent magnet and the concentration for supernatant was calculated using FAAS. The used BTCA-P-Cu-MCP was sonicated with
0.3 M NaCl for 5 min and before the next cycle, the used BTCA-P-Cu-MCP was rinsed three times with deionized water and dried in oven at 70 °C.

**Environmental water sample preparation**

Three water samples of river tap and well sources were collected in polyethylene bottle and wrapped with aluminum foil. All the water samples were filtered and stored in a refrigerator at 4 °C before analysis. The developed MSPE method was applied to the unspiked water samples (without any addition of Pb(II) ions + standard solution) and spiked water samples with three Pb(II) ions concentration levels (20, 60, and 100 μg L⁻¹). The relative recovery (RR) is calculated by the following equation:

$$\text{RR} \% = \frac{(C_{\text{found}} - C_{\text{real}})}{C_{\text{add}}} \times 100\%$$  \hspace{1cm} (5)

where $C_{\text{found}}$ refers to the concentration of the analyte after adding a known amount of standard to the real sample, $C_{\text{real}}$ is the concentration of the analyte in real sample, and $C_{\text{add}}$ represents the concentration of a known amount of standard that was spiked in the real sample (Mashkani et al. 2018).

**Results and discussions**

**Characterization of adsorbent**

**FTIR spectroscopy**

FTIR spectrometry analysis was carried out to approve the presence of characteristic functional groups as well as the interaction between the starting materials to form the synthesized compounds. Figure 2 shows FTIR spectrum of piperazine, BTCA, BTCA-P-Cu-CP, and BTCA-P-Cu-MCP. The bands appeared at 3324 and 3230 cm⁻¹ were assigned to asymmetric and symmetric stretching vibration of N–H bond in piperazine spectrum. Furthermore, the peaks at 2988 and 1277 cm⁻¹ are due to the C–H and C–N stretching vibrations respectively as Fig. 2a shows. The deprotonation of BTCA can be proven by the presence of asymmetric and symmetric stretch of C=O at 1700 and 1530 cm⁻¹ in Fig. 2b and the absence of these bands in Fig. 2c. However, two new stretches at 1581 and 1390 cm⁻¹ were observed instead, supporting the coordination of Cu²⁺ with BTCA as seen in BTCA-P-Cu-CP spectra (Fig. 2c) (Misdan et al. 2014; Tella et al. 2014; Yang et al. 2012). In addition, as shown in Fig. 2c, the presence of an absorption band at 582 cm⁻¹ indicated the formation of the Cu–O coordination bond in BTCA-P-Cu-CP. All the peaks of BTCA-P-Cu-CP (Fig. 2c) obviously observed on IR spectra of BTCA-P-Cu-MCP (Fig. 2d), although some of these adsorption bands shifted and intensity has changed. The stretching vibration peak of Cu–O in BTCA-P-Cu-MCP shifted to 596 cm⁻¹ comparing in BTCA-P-Cu-CP spectra due to the interaction between Fe₃O₄ and BTCA-P-Cu-CP as well as overlapping with Fe–O spectra. (Naeimi and Faghihian 2017a; Shi et al. 2018; Wang et al. 2015). Subsequently, all the above results reflected the successful formation of BTCA-P-Cu-CP and BTCA-P-Cu-MCP compounds.

**Crystal properties**

Powder XRD was used to determine the crystal phase, crystallite size, and degree of crystallinity of BTCA-P-Cu-CP and BTCA-P-Cu-MCP compounds. The diffraction peaks of
BTCA-P-Cu-CP (Fig. 3a) corresponded to 001, 010, 114, and 104 planes respectively. The peaks in XRD spectra of BTCA-P-Cu-MCP are almost consistent with BTCA-P-Cu-CP and the primary peak for MNPs appeared at 2 theta around 36 (Fig. 3b) revealing the successful magnetization of BTCA-P-Cu-CP (El Ghandoor et al. 2012). Based on the above results, crystal phase of BTCA-P-Cu-CP became intact after magnetization and the intensity only have changed.

The average crystallite size for each sample was estimated using Scherrer’s equation \( (D = (K \lambda)/\beta \cos \theta) \) (Afzal et al. 2016). The calculated average crystal size of BTCA-P-Cu-CP and BTCA-P-Cu-MCP was 18.8 and 19.8 nm respectively. The synthesis condition showed impact on the crystallite size, since BTCA-P-Cu-CP was synthesized at room temperature while BTCA-P-Cu-MCP at 70 °C.

Morphological and elemental analysis

Field emission scanning electron microscopy (FSEM) was used to investigate the surface morphology of the composite before and after magnetization. As it is illustrated in Fig. 4a, BTCA-P-Cu-CP has smooth open tube-like structure with an average length of 0.8 μm while BTCA-P-Cu-MCP (Fig. 4b) has wrinkle rough tube-like structure with an average length of 1.8 μm. The increased length is probably due to the different preparation methods used to prepare BTCA-P-Cu-CP comparing to BTCA-P-Cu-MCP. Furthermore, the SEM image (Fig. 4b) shows that MNPs incorporated within the BTCA-P-Cu-MCP pores as well as anchored on its surface.

CHN analysis results showed that BTCA-P-Cu-CP is composed of 45.60% C, 3.50% H, and 7.56% N. EDX analysis was used to confirm the presence of elements that cannot be detected by CHN analysis such as Fe, Cu, and O in the synthesized MNPs. BTCA-P-Cu-CP, and BTCA-P-Cu-MCP. The results showed that the MNPs composed of 75.5% Fe and 24.5% O which confirming the successful formation of pure MNPs. Furthermore, EDX analysis exhibited that BTCA-P-Cu-CP contains 8.61% Cu as well as 34.68% O. After magnetization, the analysis showed the presence Fe in BTCA-P-Cu-MCP composite in addition to Cu, C, N, and O. which directly confirmed the successful magnetization of BTCA-P-Cu-CP with MNPs.

The nitrogen adsorption–desorption isotherms was used to investigate the surface area, pore size, and pore volume for BTCA-P-Cu-CP and BTCA-P-Cu-MCP. The tabulated results (Table 1) shows that BTCA-P-Cu-MCP has higher BET surface area and pore volume values which may explained the difference amount of N\(_2\) adsorption and desorption within two compounds at a given relative pressure as seen from Fig. 5. The final N\(_2\) uptake from the profiles was found to be 6.3 cm\(^3\) g\(^{-1}\) and 20.5 cm\(^3\) g\(^{-1}\) for BTCA-P-Cu-CP and BTCA-P-Cu-MCP respectively. The higher adsorption amounts of BTCA-P-Cu-MCP justifies the role of MNPs to enhance CPs properties.

However, BJH adsorption pore size was lower in BTCA-P-Cu-MCP than in BTCA-P-Cu-CP because of adding MNPs

<table>
<thead>
<tr>
<th>Compounds</th>
<th>S(_{\text{BET}}) (m(^2)/g)</th>
<th>BET adsorption pore size (nm)</th>
<th>Pore volume (cm(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTCA-P-Cu-CP</td>
<td>5.24</td>
<td>7.5</td>
<td>0.01</td>
</tr>
<tr>
<td>BTCA-P-Cu-MCP</td>
<td>10.70</td>
<td>11.9</td>
<td>0.03</td>
</tr>
</tbody>
</table>
that occupied some CP cavities which is compatible with SEM results. As shown in Fig. 5, both sorption isotherms revealed type IV behavior with a hysteresis loop according to the IUPAC classification (Dong et al. 2014; Lee et al. 2014).

**Magnetic properties**

The magnetic behavior of MNPs and BTCA-P-Cu-MCP was assessed by a vibrating sample magnetometer (VSM) at room temperature. Figure 6 shows the magnetization curves of MNPs and BTCA-P-Cu-MCP. The hysteresis, remanence, and coercivity in magnetization curves are close to zero which indicates that both materials are supermagnetic. The results show the saturation magnetization (Ms) for MNPs and BTCA-P-Cu-MCP are 63.3 emu g$^{-1}$ and 15.4 emu g$^{-1}$ respectively. The reduction of Ms value of BTCA-P-Cu-MCP as compared to MNPs value was predicted due to BTCA-P-Cu-MCP which is non-magnetic compound. The reduction of magnetization of magnetic porous coordination polymers also has been reported by previous literature (Ke et al. 2011; Naeimi and Faghihian 2017b). However, the magnetization of BTCA-P-Cu-MCP prepared in this work was sufficient for MSPE application. BTCA-P-Cu-MCP was dispersed in water and by placing a magnet near the glass vial, the particles were easily collected as photo inset of Fig. 6 illustrates.

**Optimization of adsorption parameters**

**Effect of solution pH**

The pH of sample aqueous solutions is an essential analytical parameter that influence the adsorption of metal ions. The effect of pH in this study was investigated in the range of 4–6. As evidenced from Fig. 7a, as pH solution increased the percentage removal increased from 4 to 6 due to electrostatic interaction between metal ion and negatively charged surface of BTCA-P-Cu-MCP. At lower pH solution, there are high concentration of (H$_3$O$^+$) which were competitive for the available adsorption sites with the Pb(II) ions. As the value of pH increased, the amount of H$_3$O$^+$ would decrease, resulting in increasing the adsorption of Pb(II) ions. Figure 7b showed zeta potential analysis of BTCA-P-Cu-MCP with effects of pH range from 4 to 10 which represented that the surface charge of BTCA-P-Cu-MCP becomes more negative as pH increased. That results are probably due to deprotonation of –OH on the Cu-MCP surface as well as more deprotonation of –COOH as the acidity getting decreased (Baharin et al. 2016; Lin et al. 2014). Moreover, besides the former electrostatic effect, the results can be explained according to Hard-Soft-Acid-Base (HSAB) theory in which a strong covalent bond rapidly forming between soft acid with soft base. In this experiment, lead ions which belong to soft acids have higher attraction with soft base N in piperazine ligand and so there was N coordination in adsorption process of Pb(II) ions on BTCA-P-Cu-MCP (Wu et al. 2016; Zhang et al. 2016). Considering the self-sedimentation of Pb(II) ions at pH > 6 to form undesired precipitate (Pb(OH)$_3$ and Pb(OH)$_2$), the further experiments were carried out using a solution at pH 5.5 (Zhang et al. 2016, 2017).

**Effect of adsorbent of mass**

Adsorbent dose is one of the most important factors impacting the adsorption process of the adsorbant. The amount of BTCA-P-Cu-MCP was investigated in the range of 1–15 mg to determine the optimal amount of sorbent. As shown in Fig. 7c, the percentage removal increased with an increasing amount of absorbent dose from 1 to 5 mg and because of increasing the adsorbent surface area and the number of active sites used in adsorption. After 5 mg, the removal reached equilibrium and therefore, 3 mg of sorbent dose selected for further experiments.

**Effect of initial concentration and adsorption isotherm**

Adsorption isotherms play an fundamental role in the determination of the maximum adsorption capacity of sorbents as well as in the design of the adsorption system (Duman et al. 2016). In this study, non-linear forms of Langmuir and Freundlich isotherm models were used to analyze the experimental isotherm data. Langmuir isotherm model is based on a monolayer formation on a heterogenous surface and controlled by chemoadsorption while Freundlich isotherm model is based on multilayer adsorption on a homogenous surface and controlled by physical adsorption. The non-linear expression of Langmuir and Freundlich isotherm models are
represented by Eqs. (6) and (7), respectively:

\[ q_e = q_m K_L \frac{C_e}{1 + K_L C_e} \]  
\[ q_e = K_F C_e^{1/n} \]  

where \( C_e \) is the equilibrium concentration of remaining Pb(II) ions in the solution after removal (mg L\(^{-1}\)), \( q_e \) (mg/g) is the experimental equilibrium adsorption capacity, \( q_m \) is the maximum adsorption capacity (mg g\(^{-1}\)), \( 1/n \) is the empirical parameter related to the energetic heterogeneity (average energy of sites), and \( K_L \) and \( K_F \) (L mg\(^{-1}\)) are the Langmuir and Freundlich equilibrium adsorption constants respectively. In Langmuir equation, \( q_m \) and \( K_L \) were calculated from the intercept and the slope of plotting \( C_e/q_e \) versus \( C_e \) while in Freundlich equation, the values of \( 1/n \) and \( K_F \) were obtained from the slope and intercept of plotting \( \ln q_e \) against \( \ln C_e \).

As shown in Fig. 8, as the initial concentration of Pb(II) ions increased, the adsorption capacities \( q_e \) increases until reached equilibrium state on further increasing.

The obtained isotherm parameters are listed in Table 2. Langmuir isotherms seemed to be the best-fitting models for the experiment results as Fig. 8 shows. However, \( R^2 \) values of Langmuir and Freundlich isotherms show that both models may represent the experimental data of Pb(II) ions onto BTCA-P-Cu-MCP.

The maximum adsorption capacity \( (q_m) \) for Pb(II) ions is 582 mg g\(^{-1}\) which is higher than those reported adsorbents (Table 3). The superior fitting of Langmuir isotherm model indicated the homogeneous adsorption surface with all the adsorption sites on BTCA-P-Cu-MCP having equal adsorption affinity (Luo et al. 2014). However, since, the value of \( n \) obtained lie between 1 and 10, Freundlich model indicates favorable adsorption of Pb(II) ions on BTCA-P-Cu-MCP. Hence, based on all the data above, both physical adsorption and chemical adsorption play vital roles, which greatly

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**Fig. 7** The effect of a pH, b the zeta potential of BTCA-P-Cu-MCP at various pHs, and c dosage on the adsorption of Pb(II) ions

**Fig. 8** Adsorption isotherms for Pb(II) ions on BTCA-P-Cu-MCP by non-linear method
improve the absorptive capacity of the BTCA-P-Cu-MCP for Pb(II) ions.

Kinetic study

The adsorption kinetics of Pb(II) ions adsorption process were studied since adsorption equilibrium time is one of the most important factors for cost-effective wastewater treatment. In addition, kinetic modeling provides information for the equilibrium time and the mechanism of adsorption, such as physisorption and chemisorption as well as possible rate-controlling steps (Gupta and Balomajumder 2015). Contact time was used to carry out the kinetic study for the adsorption of the Pb(II) ions on the magnetic adsorbent. As it is represented in Fig. 9a, the adsorption capacity increased very rapidly and reached adsorption equilibrium within 5 min with 98% of Pb(II) ions has removed. The relatively fast and efficient adsorption process can be attributed to the high porosity as well as abundant of active sites on the adsorbents.

The obtained experimental data were analyzed using non-linear form of pseudo-first order and pseudo-second order as well as intra-particle diffusion models which are expressed in Eqs. 8, 9, and 10 respectively.

\[ q_t = q_e \left(1 - \exp(-K_1 \cdot t)\right) \]  
\[ q_t = \left(\frac{q_e^2}{K_2} \cdot t\right) / \left(1 + q_e \cdot K_2 \cdot t\right) \]  
\[ q_t = K_{id} \cdot t^{0.5} + C_i \]  

where \( q_t \) (mg g\(^{-1}\)), \( q_e \) (mg g\(^{-1}\)), \( K_1 \) (min\(^{-1}\)), \( K_2 \) (g/(mg min)), \( K_{id} \) (mg/g min\(^{1/2}\)), and \( C_i \) mg/g represent the amounts of the metal ions adsorbed at equilibrium, the amounts of the metal ions adsorbed at \( t \) (min), the rate constant of the pseudo-first-order model, the pseudo-second-order rate constant, the intra-particle diffusion rate constant, and thickness of the boundary layer respectively. In pseudo-first-order model, the values of \( q_e \) and \( K_1 \) can be obtained from the intercept and slope of a plot of \( \ln(q_e - q_t) \) versus \( t \) while in pseudo-second-order model, the parameters \( q_e \) and \( K_2 \) can be estimated from the slope and the intercept of the plot \( (t/q_t) \) versus \( t \) respectively. Thickness of the boundary layer \( (C_i) \) can be obtained from the intercept of plotting \( q_t \) versus \( t^{1/2} \) and the larger intercept the greater is the boundary layer effect. Experimental data with the pseudo-first order and pseudo-second order kinetic model obtained by using the non-linear method and the intra-particle diffusion models for the sorption of Pb(II) ions are shown in Fig. 9b, c respectively.

According to the presented data (Table 4) the highest \( R^2 \) value was obtained for pseudo-second order rate kinetics in comparison to pseudo-first order model. Furthermore, the calculated \( q_e \) of pseudo-second order was almost equal to the experimental \( q_e \), which suggested that the pseudo-second order fits more the experimental data than pseudo-first order model. Therefore, the adsorption of Pb(II) ions was driven more by chemisorption process occurring at exposed surface rather than physisorption process (Ahmad et al. 2017; Ding et al. 2013).

Figure 9c shows the linear plot of \( q_t \) vs. \( t^{1/2} \) is not linear over whole time range and can be separated into two adsorption stages, mass transfer and equilibrium. The first stage with a sharp slope shows that the adsorption rate is fast, and adsorption is favorable on the surface. The second part with slow slope shows that the adsorption rate is slow and intra-particle diffusion is not involved in adsorption (Ahmad et al. 2017; Ghaedi et al. 2014; Konicki et al. 2013).

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Adsorption capacity (mg g(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-MOFs/Fe(_3)O(_4)</td>
<td>219</td>
<td>(Shi et al. 2018)</td>
</tr>
<tr>
<td>Melamine-MOFs</td>
<td>205</td>
<td>(Yin et al. 2018)</td>
</tr>
<tr>
<td>Amino-functionalized MIL-101(Cr)</td>
<td>81</td>
<td>(Luo et al. 2015)</td>
</tr>
<tr>
<td>Thiol-functionalized Fe(_3)O(_4)@Cu(_3)(btc)(_2)</td>
<td>215</td>
<td>(Ke et al. 2017)</td>
</tr>
<tr>
<td>SH-Fe(_3)O(_4)/Cu(_3)(BTC)(_2)</td>
<td>198</td>
<td>(Wang et al. 2015)</td>
</tr>
<tr>
<td>UiO-66-NH2(S)NHMe</td>
<td>232</td>
<td>(Saleem et al. 2016)</td>
</tr>
<tr>
<td>BTCA-P-Cu-MCP</td>
<td>582</td>
<td>This work</td>
</tr>
</tbody>
</table>
Thermodynamic study

To investigate the nature of the Pb(II) ions adsorption, the thermodynamic parameters such as standard Gibbs free energy ($\Delta G$, KJ mol$^{-1}$), changes in standard enthalpy ($\Delta H$, KJ mol$^{-1}$), and standard entropy ($\Delta S$, KJ mol$^{-1}$ K$^{-1}$) were determined from the data obtained at different temperatures using the following equations.

$$\Delta G = -RT\ln(55.5K_c)$$  \hspace{1cm} (11)

$$\ln K_c = \frac{-\Delta H}{RT} - \frac{\Delta S}{R}$$  \hspace{1cm} (12)

where $R$ is the universal gas constant (8.314 J/mol), $T$ is absolute temperature, and $K_c$ is the thermodynamic equilibrium constant calculated as the ratio between the sorption capacity ($q_e$) and equilibrium concentration of Pb(II) ions in solution after adsorption ($C_e$); $\Delta H$ and $\Delta S$ values were determined from the slope and the intercept of the linear plot ($R^2 = 0.991$) of $\ln K_c$ versus $1/T$ respectively. As shown in Table 5, an increase in temperature increases the adsorption capacity ($q_e$); therefore, temperature provided positive effect on adsorption of Pb(II) ions on magnetic composite. That trend is

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$q_e$ (mg g$^{-1}$)</th>
<th>$\Delta G$ (KJ mol$^{-1}$)</th>
<th>$\Delta H$ (KJ mol$^{-1}$)</th>
<th>$\Delta S$ (KJ mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>13.7</td>
<td>-16.7</td>
<td>146</td>
<td>0.55</td>
</tr>
<tr>
<td>303</td>
<td>15.7</td>
<td>-20.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>16.2</td>
<td>-22.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>16.8</td>
<td>-25.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
perhaps related to decrease in viscosity and so increase in diffusion of the solution (Sumida et al. 2011). $\Delta G$ for Pb(II) ions adsorbent systems were negative values which indicate that the adsorption process is spontaneous thermodynamically and favorable at a high temperature. The positive value of $\Delta H$ indicates an endothermic nature of the adsorption, while the positive value of $\Delta S$ illustrates an increase in the degree of freedom as well as in randomness state at the solid/solution interface (Abou El-Reash 2016; Luo et al. 2014). In addition, the values of $\Delta G$ between 0 and $-20$ kJ/mol provided physisorption process, while $\Delta G$ values between $-80$ and $-400$ kJ/mol belongs to chemisorption process (Rashidi Nodeh et al. 2016).

**Optimization of MSPE preconcentration method**

The effects of various parameters (solution pH, mass of adsorbent, and contact time) on preconcentration performance of BTCA-P-Cu-MCP MSPE were investigated in adsorption section. The parameters affecting desorption condition were studied in current section. The proper selection of eluting solvent in MSPE procedure is an important factor which can result in a higher extraction efficiency (Rozi et al. 2016). Therefore, the effect of the type of desorption solvent was studied using a series of selected eluent solutions, including HCl, HNO$_3$, H$_2$SO$_4$, CH$_3$COOH, EDTA, NaCl, and thiourea. Our results showed that the acids (HCl, HNO$_3$, H$_2$SO$_4$, CH$_3$COOH) as well as EDTA decomposed the structure of MCP as reported with Fe$_3$O$_4$/IRMOF-3 and JUC-62 respectively (Hassanpour et al. 2015; Wang et al. 2014). On the other hand, the results showed that the NaCl and thiourea desorbed Pb(II) ions without any decomposition of BTCA-P-Cu-MCP structure. However, the experimental data showed that NaCl as a desorption solvent provide higher recovery for Pb(II) ions (85%) compared to thiourea (35%) and that may due to strong capability of NaCl to complex with lead ions as reported by Javanbakht et al. (Javanbakht et al. 2016). Thus, NaCl was selected as the best desorption solvent.

Desorption time was studied in the range of 2–12 min. Figure 10a shows that the recovery increased from 2 to 5 min and then no significant increasing. Since, a sonicating time of 5 min appeared to be sufficient for complete desorption. Therefore, 10-min desorption time is used in further experiments.

![Graph](image-url)
Concentration of NaCl as desorption solvent was studied in the range of 0.1–1.0 M and the results indicated that the higher recovery achieved with 0.3 M NaCl and a decrease was observed with further increase in eluent concentration as shown in Fig. 10b. That may be due to the low mass transfer of lead ions from BTCA-P-Cu-MCP to NaCl solvent at higher concentration. Therefore, 0.3 M NaCl as a desorption solvent was used in subsequent experiment.

Since the extraction efficiency depends totally on the analytes desorbed from the adsorbent, the effect of eluent volume on the recovery of Pb(II) ions was investigated using five different volumes of 0.3 M NaCl (0.5, 1.0, 2.0, 4.0, 5.0 mL). Figure 10c represents that the Pb(II) ion recovery was increased when the elution volume was increased up to 1 mL and then slightly decreased. Probably, 0.5 mL is insufficient for desorption of all the Pb(II) ions from the adsorbent surface and when the volume of elution solvent is above 1 mL, the enrichment factor is reduced. Therefore, 1.0 mL of (0.3 M) NaCl solution was chosen as the best eluent volume for further experiment.

Sample volume plays an important role in extraction process since a higher preconcentration factor can be achieved by increasing the sample to eluent volume ratio by decreasing the eluent volume and/or increasing the sample volume. Therefore, different volumes of sample solution (10–140 mL) were used to investigate the effect of sample volume on the recoveries of Pb(II) ions under optimal conditions. As shown in Fig. 10d, the Pb(II) ions recovery was found to be constant until 100 mL of sample solution volume and a decrease was observed with additional increases in sample volume. This might be due to the non-availability of the active sites of BTCA-P-Cu-MCP which are fully occupied by the analyte Pb(II) ions which indicate that the sorption breakthrough was exceeded and the adsorbent had exceeded its saturation intake (Musa et al. 2018; Raoov et al. 2014). Thus, 100 mL was selected as the optimum sample volume and the preconcentration factor was calculated as 100 for Pb(II) ions as the eluent volume used was 1 mL.

Interference studies

To validate the selectivity of the developed method, the effects of common coexisting cations and anions on the recoveries of the Pb(II) ions were studied under optimal conditions. Each experiment was repeated three times and averaged values are given as the results. The tabulated results (Table 6) that show the presence of these interfering ions at a given concentration have no significant effect on the recoveries of the Pb(II) ions. Therefore, the developed method has high selectivity toward the target analytes.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Added as</th>
<th>Recovery (%)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr3+</td>
<td>Cr(NO3)3</td>
<td>97 ± 2.7</td>
</tr>
<tr>
<td>F–</td>
<td>NaF</td>
<td>98 ± 3.2</td>
</tr>
<tr>
<td>Fe3+</td>
<td>FeCl3</td>
<td>95 ± 2.5</td>
</tr>
<tr>
<td>K+</td>
<td>KBr</td>
<td>104 ± 3.2</td>
</tr>
<tr>
<td>Ca2+</td>
<td>CaCl2</td>
<td>96 ± 2.3</td>
</tr>
<tr>
<td>CO32−</td>
<td>Na2CO3</td>
<td>98 ± 3.6</td>
</tr>
<tr>
<td>SO42−</td>
<td>Na2SO4</td>
<td>97 ± 2.8</td>
</tr>
<tr>
<td>Zn2+</td>
<td>Zn(NO3)2.4H2O</td>
<td>95 ± 3.6</td>
</tr>
</tbody>
</table>

MSPE method validation

To validate the developed MSPE method, the linearity, limit of detection, limit of quantification, and precision were assessed under the optimized conditions. Calibration curve was constructed by analysis of a series of solutions containing 0.1–100 μg L⁻¹ Pb(II) ions respectively. Table 7 shows that this method has a wide linear range with good correlation of determination (R²). The limits of detection, defined as LOD = 3 Sb/m, limit of quantification, defined as LOQ = 10 Sb/m, were 0.03 and 0.11 μg L⁻¹ respectively, where Sb is the standard deviation of 10 replicate blank signals and m is the slope of the calibration curve. The precision of the developed method was estimated by performing intra-day (from seven replicate sample preparations containing 20 μg L⁻¹ Pb(II) ions and inter-day (studied during three following days) analysis. The developed method exhibited excellent precision since the intra-day RSD% (repeatability) and the inter-day RSD% values were 1.54 and 3.43 respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linearity (μg L⁻¹)</td>
<td>0.1–100</td>
</tr>
<tr>
<td>R²</td>
<td>0.9992</td>
</tr>
<tr>
<td>LOD (μg L⁻¹)</td>
<td>0.03</td>
</tr>
<tr>
<td>LOQ (μg L⁻¹)</td>
<td>0.11</td>
</tr>
<tr>
<td>Precision</td>
<td></td>
</tr>
<tr>
<td>Intra-day (RSD%, n = 7)</td>
<td>1.54</td>
</tr>
<tr>
<td>Inter-day (RSD%, n = 3)</td>
<td>3.43</td>
</tr>
<tr>
<td>EFa</td>
<td>100</td>
</tr>
</tbody>
</table>

a Enrichment factor was calculated using EF = Vsample/Vsolvent.
Reusability of the BTCA-P-Cu-MCP

The stability and reusability were investigated because of their importance in the adsorbent practical application. Therefore, reusability studies of BTCA-P-Cu-MCP were carried out to inspect the effects of repeated adsorption–desorption cycle extractions on the adsorption capacity ($q_e$). As shown in Fig. 11, there is no obvious decrease in $q_e$ even after five cycle usage, indicating high reusability and stability efficiency of BTCA-P-Cu-MCP for Pb(II) ions extraction.

Determination of Pb(II) ions in environmental water samples

The developed MSPE method based on BTCA-P-Cu-MCP was applied to the analysis of three water samples to insure the applicability and reliability of it. The obtained results (Table 8) show the recoveries for all spiked water in the range of 93.38–100.1%, with RSD % ($n = 3$) ranging from 1.8 to 4.0%. These results indicated that the developed method is reliable and has good performance in determination of lead ions in real water samples.

Comparison with other published results

A literature review was conducted to find the previous studies for Pb(II) ions extraction using magnetic coordination polymers (MCPs) and the results are summarized in Table 9. The comparative analysis shows that the developed method MSPE has the lowest LOD, shortest extraction time, and highest adsorption capacity ($q_e$) compared to reported adsorbents (Table 9). That superiority of developed MSPE method may due to the high porosity of the adsorbent as well as the strong electrostatic force between the target Pb(II) ions and BTCA-P-Cu-MCP. Furthermore, the present MSPE method shows wide linear range, good precision (RSD), acceptable enrichment factor, and high recovery for Pb(II) ions extraction from water samples. Finally, the proposed method can be named as an environmentally friendly method since using lower and nontoxic solvents.

Proposed mechanisms of the Pb(II) ions adsorption

The high adsorption capacity in this study is due to the high porosity and the functional groups present on the surface of BTCA-P-Cu-MCP. The plausible mechanisms of the adsorption of Pb(II) ions on BTCA-P-Cu-MCP is shown in Fig. 12 and explained as follows:

Table 8 Determination of Pb(II) ions in real water samples ($n = 3$; pH = 5.5; sorbent dose = 3 mg; sample volume, 100 mL; eluent, 1 mL of 0.3 mol L$^{-1}$ NaCl)

<table>
<thead>
<tr>
<th></th>
<th>Spiked (µg L$^{-1}$)</th>
<th>Found (µg L$^{-1}$)</th>
<th>% relative recovery</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>&lt; LOQ</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>20</td>
<td>19.00</td>
<td>94.75</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>57.6</td>
<td>95.92</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>97.1</td>
<td>97.05</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Tap water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>&lt; LOQ</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>20</td>
<td>19.50</td>
<td>97.18</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>58.00</td>
<td>96.56</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>98.00</td>
<td>97.90</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Well water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>&lt; LOQ</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>20</td>
<td>19.20</td>
<td>95.66</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>56.10</td>
<td>93.48</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>101.00</td>
<td>100.93</td>
<td>1.9</td>
<td></td>
</tr>
</tbody>
</table>
1. The electrostatic attraction is the main force for the adsorption of Pb(II) ions on BTCA-P-Cu-MCP as the pH solution increased; the negative charge of BTCA-P-Cu-MCP increases as represented by Zeta potential results (Fig. 6b). Therefore, increased the electrostatic attraction results in higher Pb(II) ions removal.

2. Since Pb(II) ions is low in electrons (Lewis acid), it can make complex of coordination with electrons from Lewis base of N in piperazine, oxygen, and hydroxyl group on BTCA-P-Cu-MCP (Chen et al. 2016; Yin et al. 2016). Moreover, according to (HSAB) theory, N atom in piperazine as a kind of soft base may coordinate with Pb(II) ions (soft acid) in the adsorption process of Pb(II) ions on BTCA-P-Cu-MCP (Nabid et al. 2012).

### Conclusion

A novel copper-based magnetic coordination polymer was successfully synthesized, characterized, and applied for the removal and preconcentration of trace level of leads from several environmental water samples. The lead removal process was validated using experimental adsorption capacity, adsorption rate, and temperature effects. The results showed that the synthesized BTCA-P-Cu-MCP has high removal Pb(II) ions capacity (582 mg g\(^{-1}\)) and the adsorption behavior could be described by Langmuir and Freundlich isotherm. The sorption process was kinetically fast and reached adsorption equilibrium within 5 min. The adsorption process was spontaneous and endothermic. The intra-particle diffusion model

### Table 9  Comparison of the current work with other MCPs for the extraction of Pb(II) ions using FAAS

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Linear range (µg L(^{-1}))</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
<th>LOD (µg L(^{-1}))</th>
<th>(q_e) (mg/g)</th>
<th>EF</th>
<th>Extraction time (min)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic MOF-Pyridine</td>
<td>2.5-125</td>
<td>92-103</td>
<td>4.3</td>
<td>1.1</td>
<td>198</td>
<td>167</td>
<td>14</td>
<td>(Sohrabi et al. 2013)</td>
</tr>
<tr>
<td>Fe(_3)O(_4)@TAR/HKUST-1</td>
<td>2-200</td>
<td>92-112</td>
<td>6.4</td>
<td>0.8</td>
<td>185 ± 7</td>
<td>200</td>
<td>10</td>
<td>(Ghorbani-Kalhor 2016)</td>
</tr>
<tr>
<td>SH-Fe(_3)O(_4)/Cu(_2)(BTC)(_2)</td>
<td>1-20</td>
<td>97-104</td>
<td>2.4</td>
<td>0.29</td>
<td>198</td>
<td>100</td>
<td>15</td>
<td>(Wang et al. 2015)</td>
</tr>
<tr>
<td>Fe(_3)O(_4)-ethylenediamine/MIL-101(Fe)</td>
<td>2.5-250</td>
<td>90-106</td>
<td>4.9</td>
<td>0.8</td>
<td>198</td>
<td>238</td>
<td>15</td>
<td>(Babazadeh et al. 2015)</td>
</tr>
<tr>
<td>Fe(_3)O(_4)@dithizone/MMOF</td>
<td>4-140</td>
<td>92-102</td>
<td>4.3</td>
<td>1.2</td>
<td>213</td>
<td>128</td>
<td>13</td>
<td>(Taghizadeh et al. 2013)</td>
</tr>
<tr>
<td>BTCA-P-Cu-MCP</td>
<td>0.1-100</td>
<td>94-101</td>
<td>1.8-4.0</td>
<td>0.03</td>
<td>625</td>
<td>100</td>
<td>5</td>
<td>Current work</td>
</tr>
</tbody>
</table>

![Fig. 12](image-url) Proposed mechanism of interaction between Pb(II) ions and BTCA-P-Cu-MCP (proposed structure according to characterization results)
proved that adsorption was controlled by two steps. After five regeneration cycles, the adsorption capacity remained almost intact. The proposed MSPE method provided lowest LOD (0.03 μg L−1) with wide linear range (0.1–100 μg L−1). Furthermore, it was successfully used for preconcentration of trace lead in different environmental water samples with high recovery (94–101%). Therefore, fast extraction, good regeneration capability, and using non-toxic solvent made this adsorbent economical and environmentally friendly.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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