Removal of heavy metals from artificial metals contaminated water samples based on micelle-templated silica modified with pyoverdin I

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Abstract

The micelle-templated silica (MTS) was firstly chemically modified with 3-glycidoxypropyl-trimethoxysilane (GPTMS) before immobilized with pyoverdin I. The characteristics of pyoverdin I-anchored onto the modified MTS were investigated using fluorescence, infrared spectra and scanning electron microscopy. The specific surface area of all materials was calculated by Brunauer, Emmett and Teller (BET) method using nitrogen isotherm adsorption data. As the results, the surface area of commercial silica gel decreased from 609.2 to 405.4 m²/g, it indicated that the pyoverdin I could be immobilized onto the surface of silica solid support. This adsorbent was used for extraction of Fe(III), Cu(II), Zn(II), and Pb(II) in artificial metals contaminated water. Experimental conditions for effective adsorption of trace levels of metal ions were optimized with respect to different experimental parameters using batch procedure. The optimum pH value for the removal of metal ions simultaneously on this adsorbent was 4.0. Complete desorption of the adsorbed metal ions from the adsorbent was carried out using 0.25 mol/L of EDTA. The effect of different cations and anions on the adsorption of these metals on adsorbent was studied and the results showed that the proposed adsorbent could be applied to the highly saline samples and the sample which contains some transition metals.

Key words: micelle-templated silica; pyoverdin I; removal of heavy metals

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Introduction

The contamination of heavy metals has increased in the environment, especially in the agricultural fields and industrial areas. Heavy metals are not biodegradable and thermodegradable, and can be harmful to human, plants and animals. Therefore the selectively extraction technique for heavy metals in environmental samples is becoming more and more important (Liu et al., 2005). Of all the remediation methods used, ion exchange has been widely used and show high performances but generally poor selectivities towards different metal ions. Many types of ion-exchange resins and chelate resins such as cellulosic derivatives (Lee et al., 1997), polyurethane foam (Moyano et al., 1999), polystylene, polyvinyl resin and silica gels were used for solid phase extraction. Nowadays, intensive studies have been performed to find new effective sorption materials or to modify their adsorbents. In several researches, silica has been adopted as a good alternating support for chelating substrate to be used as an adsorbent (Guo et al., 2004; Kim et al., 2005). This is due to the availability of many silylating agents and silica phases of large specific surface area. Because of the ion-exchange of the metal at the silanol group, it was very difficult to extract metal ions and/or metal-chelates which were only generated in a strong acid aqueous solution. To overcome this problem, physical or chemical modification of a silica gel surface via binding with some chelating agents, is a usually procedure for incorporating some selectivity in such phase (Khorrami et al., 2006). The modification of surface of silica gel can be done using organosilane reagent and then immobilized with biological chelating agent. The organosilane reagent was immobilized onto the silica surface to convert a new organofunctional surface that acquires the organophilic properties (Jal et al., 2004). The discovery of mesoporous silicates has greatly expanded the possibilities for the design of new nanostructured materials, micelle-templated silica (MTS) constitute excellent mineral supports for the preparation of inorganic-organic hybrid materials by grafting organic chains onto their surface through silylation. The MTS have evidenced the involvement of the hydrophobic sites during the silanation procedure through preservation of the hydrophilic patches of the MTS (Pierre et al., 1999). Therefore, according to this hypothesis, the environment of the grafted organic moieties would mainly consist in residual interacting silanol groups. Further end-capping of
the epoxy-Si surface with cetyltrimethylammonium bromide (CTAB) minimized the possible interactions between the anchored catalytic sites and the uncovered surface and, as a consequence, increased their catalytic activity. The methods were used for the activation of silica involves the formation of an intermediate silane-coupling agent, which is chosen according to the connecting group of the organic ligand. The ligand has an aminoaalkyl group attached to the chelating moiety. The activation of the silica surface with oxirane groups is the most adequate for bonding the ligand by nucleophilic attack and epoxy ring opening (Esteves et al., 2005). In addition, some applications of chelating agents loaded on silica surface are N-alkyl dithiocarbamate for the preconcentration of such cations as Hg(II), 2-amino-1-cyclopentane for the extraction of Pb and Hg (Gurnani et al., 2003). Several researches have been interested in organic chelating agent especially siderophore. Siderophores are compounds produced by some microorganisms under iron-starved conditions. Pyoverdins, water soluble molecule, are siderophores produced by Pseudomonas bacteria. They consist of an 8-hydroxyquinoline derivative, which forms a fluorescent chromophore and an octapeptide, which contains two residues of N-hydroxynornithine. They provide one bidentate ligand for Fe(III), a peptide chain including 6 to 12 L-, D-, and uncommon amino acids such as OH-ornithine (which tend to form a cycle), providing two bidentate sites and a small dicarboxylic acid, or its monoamide. Pyoverdins are powerful chelator of Fe(III), which is bound with a stoichiometry of 1:1 and stability constant of approximately 1024 L/mol at neutral pH (Visca et al., 1992). They have shown to be high affinity for a variety of metal ions concerned such as Cd(II), Cu(II), Pb(II), Zn(II), In(III), Al(III), and Ga(III), but its stability constants are lower than that of with Fe(III).

For these reasons, the aims of the present work were to use pyoverdin I as an alternative biological chelating agent, which immobilized onto the modified micelle-templated silica surface for improving the selectivity with some metals. Finally, the feature characteristic of this synthesized material was investigated by various techniques, including spectrofluorophotometry, IR, SEM and nitrogen adsorption isotherm.

1 Materials and methods

1.1 Apparatus and pyoverdin I production

All fluorescent measurements were carried out on an RF-5301PC recording spectrofluorophotometer (Shimadzu, Japan) equipped with 1.0 cm quartz cell. An Optima 2100 DV inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elemer, USA) was used for all metal-determinations. The operation conditions and the wavelengths are summarized in Table 1.

In this study, Pseudomonas aeruginosa was used for pyoverdin I production in sucrose-asparagine (SA) medium. One liter of the medium containing di-potassium hydrogen phosphate, 1.0 g; sucrose, 10.0 g; and L-Asparagine anhydrous, 4.0 g was used. The medium was adjusted to be pH 6.5 and autoclaved. After that, 1 mL of 10 mg/L of sterilized magnesium sulfate was added into this medium. The medium was inoculated with the previous subculture of P. aeruginosa and the shaken by magnetic stirring at ambient temperature for 20 h. After precipitation of proteins, neutralization with 1.0 mol/L NaOH or 1.0 mol/L HCl solution and centrifugation for 20 min at 3500 r/min, a yellow-green supernatant was obtained. The isolation was carried out on column chromatography with an Amberlite XAD-16 resin and further purified using CM Sephadex C-25 and Bio-Gel P-2 columns. The separated fraction was eluted, concentrated and lyophilized (Ruangviriyachai et al., 2000). After that, the structural elucidation of the purified fraction was identical to pyoverdin I by Budzikiewicz et al. (2000) using spectroscopic methods. It comprised of an amino acids in peptide chain (L-ornithine, L-threonine, L-lysine, D-serine, L-arginine), a fluorescent multifunctional chromophore (pyoverdins) and side chain (succinic acid). The detection of pyoverdin I was carried out using a photodiode array (PDA) at 254 and 400 nm and fluorescence detection (Waters) at 460 nm (λex 400 nm), respectively.

Metal ion (1 mg/mL) solutions were prepared by dissolving analytical grade salts in deionized water with addition of 1 mg/L of HCl and further diluted daily prior to use. Silica gel (80–120 mesh, Carlo Erba, Italy) and 3-glycidoxypropyl-trimethoxysilane (GPTMS, Sigma, USA) were used to prepare the ion-imprinted functionalized adsorbent.

1.2 Synthesis of the adsorbent

The synthesis of the MTS was prepared according to the procedure described by Ottaviani et al. (2004). In brief, the reactants were added under stirring at room temperature in the following order: deionized water, sodium hydroxide (Carlo Erba, Italy), cetyltrimethylammonium bromide (CTAB) (Merck, Germany), trimethyl-benzene (TMB) (Carlo Erba, Italy) and SiO2 (Carlo Erba, Italy) with a molar ratio of 20:0.25:0.1:1:3:1. The mixture was refluxed at 115°C for 3 h, then filtered, washed with distilled water till neutralization and dried at 115°C. This material was then calcinated by a thermal treatment at 550°C for 8 h.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
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<td>Radio frequency power (kW)</td>
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</tr>
<tr>
<td>Carrier gas (Ar) flow rate (L/min)</td>
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</tr>
<tr>
<td>Auxiliary gas (Ar) flow rate (L/min)</td>
<td>1.0</td>
</tr>
<tr>
<td>Coolant gas (Ar) flow rate (L/min)</td>
<td>14</td>
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<tr>
<td>Nebulizer flow (psi)</td>
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</tr>
<tr>
<td>Pump rate (r/min)</td>
<td>100</td>
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<tr>
<td>Observation height (mm)</td>
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<tr>
<td>Integration time (s)</td>
<td>20</td>
</tr>
<tr>
<td>Wavelength (nm)</td>
<td>Fe 259.940, Cu 324.754, Zn 213.856, Pb 220.353</td>
</tr>
</tbody>
</table>
The grafting of the MTS with 3-glycidoxypropyltrimethoxysilane (GPTMS) from Sigma-Aldrich, USA, was carried out according to the procedure of Brunel et al. (1993). A 1.0 g of the MTS was activated overnight at 180°C. After that, a 1.25 mL of GPTMS and 20 mL of toluene (J. T. Baker Chemical, Philippine) were added. The mixture solution was stirred for 90 min at 70°C, then refluxed for 1 h 30 min at 130°C, filtered and washed with toluene and then diethyl ether (VWR International, England). The MTS-1 was then dried overnight at 160°C (Jal et al., 2004).

The practical immobilization of pyoverdin I onto the surface of the MTS-1 was described by Renard et al. (2005). A 3.0-g of MTS-1 was activated at 130°C for 1 h and was then dispersed in 40 mL of dimethylformamide (DMF; Asia Pacific Specially Chemical, Australia) before adding 25 mg of lyophilized pyoverdin I. The mixture was refluxed under stirring for 48 h at 60°C, filtered and washed with deionized water and the mixture solution of water/ethanol (1:1, v/v) and finally dried overnight at 60°C. The immobilized pyoverdin I onto the surface of the MTS-1 was called MTS-2. The MTS-2 gives a yellow-green powder and blue fluorescence pigment under UV light. The techniques used to investigate the MTS-2 surface were fourier transform-infrared spectrometry (FT-IR, Perkin Elmer, Germany), scanning electron microscopy (SEM, LEO instrument, Germany) and nitrogen adsorption isotherm (Quantachrom Instruments, USA). Proposed structure of the MTS, MTS-1, and MTS-2 are shown in Fig. 1.

1.3 Solid phase extraction studies and analysis procedures

In view of our objectives, the parameters including the pH of artificial metals solution, type and concentration of eluent, time of stirring and mass of adsorbent were studied to evaluate their effect on the extraction of the metals studied. All experiments were conducted by batch procedure.

1.3.1 Effect of pH of artificial metals contaminated water samples

The pH value of the sample solution plays an important role in metal sorption. Therefore, this study was conducted in triplicate by changing the pH from 2.0 to 6.0. Adsorbent 200 mg was transferred into 10 mL of each artificial metal solution at concentration of 5 mg/L. These mixtures were then shaken using a rotary shaker for 30 min at room temperature. And then, the adsorbed metal ions were extracted from adsorbent using 1.0 HNO₃ as an eluent.

1.3.2 Effect of eluent type and its concentration

The elution condition was studied by batch procedure where two types of eluents at various concentrations have been applied to select a proper for the retained metals extracted. Quantitative recoveries were obtained by using 1 mol/L HNO₃ and 1 mol/L EDTA for analytes. The MTS-2 adsorbent was added in 10 mL of the artificial metal sample (5 mg/L) and shaken for 30 min, obtained the adsorbed metal adsorbent. The adsorbed metal adsorbent was washed with water and treated by a rotary shaker (250 r/min) with 10 mL of each eluent at room temperature for 30 min. Each mixture solution was filtered and determined the quantity of metal ions by the ICP-OES. Finally, this adsorbent was reused by washing with deionized water and dried at 50°C for 2 h.

Effect of concentrations of EDTA and HNO₃ used were also examined in the range of 0.25–1.00 mol/L and the procedure was the same as mentioned above. The results of the effect of eluent type and its concentration are summarized in Table 2.

1.3.3 Effect of shaking time on the metals removal

In order to determine the contact time required to reach equilibrium, batch sorption dynamic experiments were performed. The MTS-2 adsorbent (300 mg) was mixed with 1.0 mL of 5 mg/L metal ions and 9.0 mL of acetate buffer (1.0 mol/L NaOAc, pH 4.0). The adsorption time was varied from 0 to 60 min. All these mixture were shaken using rotary shaker (250 r/min) at room temperature. And then, the adsorbed metal ions were extracted from adsorbent using 0.25 mol/L EDTA as an eluent.

1.3.4 Effect of adsorbent mass on the removal of some metals

In order to test the adsorption of adsorbent mass, the adsorption potential of the commercial silica gel and the MTS-2 were studied by varying the amount of these adsorbents from 50 to 300 mg. Each adsorbent mass was transferred into a 25-mL Erlenmeyer flask containing 10 mL of 5 mg/L of each artificial metal solution at pH 4.0 and shaken at 250 r/min for 20 min. And then, the adsorbed metal ions were extracted from adsorbent using 0.25 mol/L EDTA.

1.4 Effect of some interfering species

The solid-phase extraction of other metal ions that do not form a chelate with pyoverdin I was studied. 50-fold Cr(NO₃)₂, 500-fold MgSO₄ and Na₃PO₄ and 200-fold KCl

![Fig 1](https://example.com/fig1.png) Proposed structures of MTS, MTS-1, and MTS-2 (Renard et al., 2005).
and Ca(NO₃)₂ were used. The experiment was carried out using optimum condition as following; 0.25 mol/L EDTA as eluent, pH of metals at pH 4.0, time for extract at 30 min and 200 mg of adsorbent mass was used.

2 Results and discussion

2.1 Study on the complexes formation of pyoverdin I and some metals

The quenching fluorescence of pyoverdin I was used to investigate the complexes formation of pyoverdin I and some heavy metals. An emission at 460 nm for pyoverdin I and decreased in fluorescence intensity for its metal complexes were observed as illustrated in Fig. 2. The quenching of fluorescence by metal complex shows that the metal was bound to the peptide-chromophore. When compare the emission spectra of each metal bound to the pyoverdin I, it was found that the order of metal ions for the quenching of fluorescence intensity of the pyoverdin I was: Fe(III) > Cu(II) > Zn(II) > Pb(II). Therefore, it is important to note that, the fluorescence quantum yield is strongly affected by the type of metal in which the pyoverdin I are complexed. For this reason, pyoverdin I was used to immobilize onto MTS for improving selective binding and extraction of these metal ions.

2.2 Characterization of the adsorbents

2.2.1 FT-IR spectra

The modified silica gel was confirmed by IR analysis and the results are shown in Fig. 3. As shown in Fig. 3 line b, the major chemical group of commercial silica gel appeared broad band near 3460 cm⁻¹, which was the silanol group. The bending vibrational peak for H–O–H is shown at 1633 cm⁻¹. The predominant transmittance peak at 1088 cm⁻¹ was due to siloxane bond (Si–O–Si). The absorption peak between 1000 and 700 cm⁻¹ could be attributed to vibration modes of the gel network (Esparrza et al., 2005). In case of IR spectrum of pyoverdin I (Fig. 3 line a), it appeared broad band at 3284 cm⁻¹ in the region of hydroxyl OH stretching. This may include absorption due to the presence of N–H stretching group. However, the overlapping of C–H stretching band that are characteristics of alkyl functional groups occurs between 2850 and 2980 cm⁻¹. Therefore, the absorption band near 2933 cm⁻¹ may be the presence of alkyl moiety in the pyoverdin I structure. The intensity band near 1661 and 1543 cm⁻¹ related to C=O and C=C stretching (cyclic or conjugated). Moreover, the peak near 1456 cm⁻¹ assigned to C–O stretching. A weak absorption peak at 1410 cm⁻¹ may be the CH₃ and the absorption peak found near 1287 cm⁻¹ may correspond to C–N stretching (aromatic). Finally, the weak intensity peak near 1071 cm⁻¹ was due to the stretching of C–NH₂ and the broad band occurred in the range of 900–500 cm⁻¹, indicating a typical aromatic ring. For IR spectrum of the MTS-2, the absorption broad band at 3468 cm⁻¹ indicating OH group on surface may also include the absorption due
to the presence of N–H group. The absorption band in the range of 3000–2800 cm$^{-1}$ may presence alkyl moiety in the structure of pyoverdin I. Some additional peaks including sharp peaks at 1655 and 1536 cm$^{-1}$ correspond to C==O and C==C stretching (Renard et al., 2005). The predominant transmittance peak at 1087 cm$^{-1}$ was due to siloxane bond (Si–O–Si). A band assigned to Si–O stretching of silanol groups shifts from 800 to 796 cm$^{-1}$. A small peak at 2950 cm$^{-1}$ corresponds to CH2 stretching due to aliphatic groups of pyoverdin I chains was shown in the FT-IR spectrum (Fig. 3 line c). Consequently, the above analysis of IR spectra suggests that pyoverdin I can be immobilized onto the MTS-1.

2.2.2 Scanning electron microscopic (SEM) photographs of the adsorbents surface

In order to evaluate the surfaces of particles before and after immobilization, the SEM analysis of commercial silica gel (Fig. 4a) was compared with the MTS-1 (Fig. 4b) and MTS-2 (Fig. 4c). After the pyoverdin I immobilized onto the MTS-1, the presence of the pyoverdin I did not seem to play a crucial role in the final structure of commercial silica gel but some changes are observed.

2.2.3 Surface area analysis of the adsorbents

The silica surface is a major factor contributing to the separation technique in chromatography. Geometry of the surface defines the accessibility of adsorption sites. The surface area of commercial silica gel, the MTS-1 and the MTS-2 were calculated through the BET equation (Fig. 5). For this experiment, the surface area of the commercial silica gel ($S_{BET}$) and pore diameter ($D$) were 540.5 m$^2$/g and 7.2 nm, respectively. After the MTS was synthesized and then grafted with GPTMS, called the MTS-1 with surface area ($S_{BET}$) and pore diameter ($D$) were 381.4 m$^2$/g and 3.6 nm, respectively. The immobilization of pyoverdin I onto the surface of the MTS-1, the hydrogen bonding between silanols and pyoverdin I would completely react between the epoxide and pyoverdin I. Any the pyoverdin I, unreacted with epoxide and hydrogen bonded to the remaining silanols, will be removed during the washing steps. Hence, the formation of the pyoverdin I leaves free amino group on the peptide backbone. This amino group reacts covalently with the epoxy group of the spacer during the anchoring process. As the result, the surface area ($S_{BET}$) and pore diameter ($D$) of the MTS-2 were 360.2 m$^2$/g and 3.0 nm, respectively and can be classified as mesoporous material. It is expected that bonded pyoverdin I may also occupy a volume inside the pore space of silica as a result decreased in original pore volume of silica is expected. A corresponding decrease in adsorbent surface area and average pore diameter can also be assumed (Renard et al., 2005). Moreover, the depression of the surface area of the MTS-1 after incorporation with pyoverdin I was due to the fact that the adsorption of nitrogen molecules on the surface blocked by the presence of pendant group, thus resulting in the depression of the surface area of the MTS-1. These results confirmed that the pyoverdin I can be immobilized onto the MTS-1 solid support.

2.3 Solid phase extraction and analysis procedures

2.3.1 Effect of pH on artificial wastewater samples

The pH of sample has an influence on the adsorption efficiency. The precipitation of some metals is occurred when the pH value was adjusted to alkaline condition, that the soluble metal ions were changed to insoluble metal hydroxides form. Therefore, pH of the sample was studied over the pH range varying from 2.0 to 6.0. Results obtained are plotted in Fig. 6, which show that the sorption of metals on the surface of adsorbent is highly pH dependent. The quantitative extraction ($N = 95\%$) could be obtained from pH 4.0 to pH 4.5. In case of Fe(III), the MTS-2 adsorbent...
does not present any extracting properties at pH higher than pH 5.0. These may be due to the precipitation of Fe(III). To determine these elements simultaneously, pH 4.0 was chosen for all experiments.

2.3.2 Effect of eluent type and its concentration on the desorption process of the adsorbent

Table 2 shows the effect of eluent types and concentration of eluting on the metals removal after separation at pH 4.0. As compared to the eluent types at equal concentration, EDTA is of better leaching efficiency of the investigated metal ions from the ion exchanger than HNO₃. The results showed that the percentage elution depend on the concentration of the eluents. However, the molar concentration of the HNO₃ and EDTA was sufficient to obtain maximum removal but the latter is recommended for applications due to high percentage removal. In addition, the pyoverdin I on the surface of the MTS-2 may be destroyed with high concentration of HNO₃ in the desorption process. The minimum concentration of EDTA was approximately 0.25 mol/L, which showed good elution efficiency that nearly 98% elution is achieved for Fe(III) removal. Hence, 0.25 mol/L EDTA was used throughout all experiments.

2.3.3 Effect of equilibrium time on the removal of some metals

The equilibrium time on adsorption of some metals from artificial metals solution by using adsorbent is normally assumed to be controlled by physico-chemical monolayer process. The results indicated that the removal of metal ions on both adsorbents increasing when the equilibrium time of the removal was increased in range from 0 to 60 min. Maximum removal of metal ions on the adsorbents was obtained at equilibrium time 30 min. The results are shown in Fig. 7.

2.3.4 Effect of the adsorbent mass on the removal of some metals

To test the effect of extractant mass on quantitative retention of the analytes, different amounts of adsorbents were added into solutions following the batch procedure. The artificial metal solution at concentration 5 mg/L (pH 4.0) was adsorbed onto the surface of commercial silica gel and the MTS-2 adsorbents. The maximum adsorption of Fe(III), Cu(II), Pb(II), and Zn(II) were obtained when mass of adsorbent at 200 mg was used as follows: 97.32%, 90.74%, 37.51%, and 47.78%, respectively. Thereby, 200 mg of the MTS-2 adsorbent was selected for further studies. The results are presented in Fig. 8.

2.4 Effect of some interfering species

In order to evaluate the selectivity of the sorbent for extraction and determination of these metals, interference of different cations and anions on the percentage removal of Fe(III), Cu(II), Zn(II), and Pb(II) were investigated. This study showed that the presence of all ions (Mg(II), Na(I),

![Fig. 5](image1)

Fig. 5 Nitrogen adsorption isotherms of the commercial silica gel (line a), the MTS-1 (line b), and the MTS-2 (line c).

![Fig. 6](image2)

Fig. 6 Effect of pH of artificial metals contaminated water samples on the percentage removal of some metals from artificial metals solution using the MTS-2.

![Fig. 7](image3)

Fig. 7 Effect of shaking time on the percentage removal of heavy metals.

| Table 2 Effect of concentration of eluents on the percentage removal of metal ions (n = 3) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Eluent type     | Fe(III) Removal (%) | Cu(II) Removal (%) | Zn(II) Removal (%) | Pb(II) Removal (%) |
| EDTA (mol/L)    | 0.25 | 98.80 ± 2.0 | 97.35 ± 1.8 | 96.45 ± 2.5 | 87.45 ± 1.8 |
|                  | 0.50 | 98.20 ± 1.2 | 97.90 ± 2.5 | 96.30 ± 3.2 | 87.35 ± 2.9 |
|                  | 0.75 | 98.89 ± 1.4 | 96.55 ± 2.7 | 96.74 ± 3.0 | 86.20 ± 2.1 |
|                  | 1.00 | 98.95 ± 1.7 | 97.82 ± 3.5 | 96.20 ± 1.5 | 87.42 ± 2.6 |
| HNO₃ (mol/L)     | 0.25 | 46.20 ± 2.5 | 48.45 ± 2.6 | 42.45 ± 2.5 | 83.74 ± 3.2 |
|                  | 0.50 | 68.75 ± 3.2 | 62.20 ± 2.5 | 62.20 ± 1.6 | 83.53 ± 3.0 |
|                  | 0.75 | 87.46 ± 1.5 | 96.70 ± 3.0 | 96.20 ± 2.2 | 82.95 ± 2.4 |
|                  | 1.00 | 97.80 ± 1.3 | 98.53 ± 2.8 | 98.20 ± 1.8 | 83.15 ± 2.1 |
|                  | 2.00 | 98.15 ± 1.5 | 98.48 ± 2.1 | 98.05 ± 1.5 | 82.87 ± 2.5 |
Table 3  Effect of interference ions on the removal of 1.0 mg/mL heavy metals by the adsorbent followed by elution with 0.25 mol/L EDTA

<table>
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<th>Interference ion</th>
<th>Concentration (mg/mL)</th>
<th>Fe(III) Removal (%)</th>
<th>Cu(II) Removal (%)</th>
<th>Zn(II) Removal (%)</th>
<th>Pb(II) Removal (%)</th>
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<tr>
<td>MgSO₄</td>
<td>500</td>
<td>98.30 ± 1.5</td>
<td>95.75 ± 2.2</td>
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<td>83.25 ± 3.5</td>
</tr>
<tr>
<td>Na₃PO₄</td>
<td>500</td>
<td>97.74 ± 2.5</td>
<td>96.47 ± 3.5</td>
<td>94.95 ± 1.9</td>
<td>82.48 ± 3.1</td>
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<tr>
<td>Ca(NO₃)₂</td>
<td>200</td>
<td>98.64 ± 2.7</td>
<td>97.26 ± 2.8</td>
<td>94.20 ± 3.0</td>
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<tr>
<td>Cr(NO₃)₃</td>
<td>50</td>
<td>96.86 ± 2.9</td>
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<td>KCl</td>
<td>200</td>
<td>98.57 ± 1.8</td>
<td>95.93 ± 3.1</td>
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Fig. 8 Effect of the MTS-2 adsorbent mass on the percentage removal of some metals.

Ca(II) and K(II)) which were found in natural water had no effect on the percentage removal of the metal studied. These results show that the proposed adsorbent could be applied to the highly saline samples and the sample which contains some transition metals at the tolerable levels given in Table 3. These obtained results are in good agreement with these obtained by Palanche et al. (1999).

3 Conclusions

Micelle-templated silica modified with pyoverdin I was established for removal of Fe(III), Cu(II), Pb(II), and Zn(II) in artificial metals contaminated water samples. The adsorbent showed a high selectivity towards Fe(III), Cu(II), Pb(II), and Zn(II) over other ions studied. The sorption behavior of this adsorbent depends upon the species, the pH of the metal solution, the mass of adsorbent used and also time for adsorption. The results obtained show that the MTS-2 adsorbent can be considered, as an alternative treatment facility of an existing metals removal technology.

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