Synthesis of sol-gel silica chemically bonded with cyanex 272 for the removal of Cu(II), Ni(II), and Zn(II)

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Abstract This article reported on the synthesis of SSCBB, a new solid-phase, sol-gel silica chemically bonded with [bis (2,4,4-trimethylpentyl) phosphinate], (BTMPP, anion of Cyanex 272) prepared with a sol-gel method, and its application as a reusable solid-phase sorbent for the selective removal of Cu(II), Ni(II), and Zn(II). The synthesized SSCBB was characterized by FTIR, EDX, SEM, BET, TGA, and DSC. To evaluate its extraction performance, various parameters such as equilibration time, pH of the aqueous phase, solid to liquid ratio, initial copper ion concentration and reusability of SSCBB were studied. Equilibrium time was found to be 60 min for all metals and almost 100% extraction occurred at a pH of 4.0, 6.0, and 8.8 for Zn(II), Cu(II), and Ni(II) extraction, respectively. The maximum extraction capacity was found to be 0.2 mmol of Cu(II) per gram of SSCBB. Moreover, it was also regenerated and reused for subsequent recovery in ten cycles. The uptake performance of regenerated SSCBB after ten regeneration cycles was found to be the same as the freshly prepared SSCBB. Finally, based on the results, a proposed flow sheet for the removal of Cu(II), Ni(II), and Zn(II) was provided.

Introduction

The Synthesis of a solid-phase extractor for the removal of metal ions from aqueous waste is gaining popularity for its diverse potentialities in applications. Many industrial processes such as mining, coating and metal surface finishing, battery and steel manufacturing, electroplating, electrolysis, fertilizer, pigments, automotive, aeronautical, photography, printing circuits, tanneries and paints discharge large quantities of wastewater containing heavy metal ions into environment [1, 2]. The increasing level of heavy metals in wastewater represents a serious risk to human health and ecological systems because they are non-biodegradable and can be accumulated in living tissues, causing various diseases and disorders [2]; therefore they must be removed before discharge. Several methods have been used for the removal of metals from aqueous media [3–8]. Among them solid-phase extraction has become known as a potential tool because it has several advantages over other techniques, including stability and reusability of the solid phase, easiness of separation and no need for organic solvents [9].

Various solid-phase extractors have been prepared by the functionalization of organic chelating reagents with different solid supports [10–15]. Silica gel is one of the most successful solid supports, because it does not swell or shrink as does polymeric resin [16]. Silica gel, functionalized with various organic groups either physically or chemically, has been used for removal of metal ions from aqueous media [17–22]. However, physical immobilization has some limitations; organic groups could be leached out, but be difficult to reuse [17]. This limitation can be overcome by using chemically modified silica materials. Most researchers have been synthesizing chemically functional solid-phase extractors using granular silica gel as a solid support, but there are very few works that have been reported on the synthesis of solid-phase extractors by chemical bonding of functional groups with silica using the sol-gel method [23–27]. BTMPPA [bis (2,4,4-trimethylpentyl) phosphinic acid] (Cyanex 272), a phosphorous-based acidic extractant, has been effectively used in solvent extraction [28, 29]. However, the synthesis of sol-gel silica chemically bonded with

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BTMPP (anion of BTMPPA) by the sol-gel method and its extraction behavior have not been studied yet.

In this present work noble solid-phase extractor sol-gel silica chemically bonded with BTMPP (SSCBB) was prepared by using the sol-gel method. This article also describes the extraction behavior of Cu(II), Ni(II), and Zn(II) from aqueous solution by this solid phase in batch mode.

Experimental

Reagents and apparatus

BTMPPA was supplied by Cytec Industry (Canada). Tetraethoxysilane (TEOS) and 3-chloropropyltryethoxysilane (CPTS) were purchased from Aldrich Company, USA. Solutions of Cu(II), Ni(II), and Zn(II) sulfate were prepared by de-ionizing water with reagent grade materials. All other chemicals used were analytical grade.

A Perkin-Elmer (Model AAnalyst 700) atomic absorption spectrometer (AAS) was used where acetylene was used as the fuel gas and air as the oxidant for the measurement of metal concentration. A digital pH meter and a wrist-action flask shaker (Model SF1, Stuart Scientific) were used to control the pH of the aqueous phase and to shake the phases. Micrographs and elemental analysis of SSCBB were obtained by SEM and EDX (JEOL JSM–6460LA) using a voltage of 20 Kv. The surface area, pore diameter and pore volume were determined according to BET and BJH methods from N_2 sorption isotherm using micrometric (Tristar 3000) surface area and porosity analyzer. Particle size was determined by a Malvern particle sizer analyzer (Mastersizer 2000). TG-DTA curves were recorded with a thermal analysis instrument (TG/DTA PerkinElmer Instruments, Pyris Diamond), by heating from room temperature to 900 °C at a heating rate of 10 °C min^{-1} in N_2 atmosphere, taking 2.983 mg of SSCBB and 2.864 mg of blank silica samples. DSC data for 7.0 mg of SSCBB and blank silica were recorded with differential scanning calorimeter (TA, Q10) from room temperature to 550 °C at a heating rate of 10 °C min^{-1} in N_2 atmosphere. An FTIR spectrometer (Perkin Elmer Spectrum RX1) was used to obtain the infrared spectrum with KBr pellets in a 4,000−400 cm^{-1} region, with a resolution of 4 cm^{-1}.

Synthesis of sol-gel silica chemically bonded with BTMPP (SSCBB)

BTMPPA and sodium hydroxide were mixed in 100 mL of toluene and mechanically stirred for 24 h at room temperature, which yielded Na-BTMPP. To this solution CPTS was added and the mixture was kept under reflux for 24 h in an oil bath maintaining a temperature of 50–60 °C, synthesized a compound, BTMPP, bonded to CPTS by displacing chlorine with sodium. The amounts of BTMPPA, sodium hydroxide, and CPTS added in the mixture were stoichiometric. Then toluene was allowed to evaporate and the product was used as organic precursor in the gelation process. In this solution 6 mL of TEOS, 10 mL of ethanol and water containing ammonium hydroxide was added while stirring. The gelation occurred in the basic environment within an hour. The gel was aged for 10 days and then washed with water and ethanol several times, dried at room temperature and used for extraction. After preparation, 1 g of SSCBB was decomposed with 10 mL of concentrated H_2SO_4 for the purpose of phosphorous determination [30]. The content of phosphorous in SSCBB was estimated by ammonium molybdate spectrophotometric method, where sodium sulfide was used as a reducing agent [31]. For comparison purposes, blank silica was prepared using the method described elsewhere [17].

Extraction studies

Extraction of metal ions from the aqueous solution by SSCBB was carried out using a batch process. SSCBB was shaken with a metal ions solution containing 0.1 molL^{-1} $\left[SO_4^{2-}\right]$ and 0.25 molL^{-1} [Ac$^-$], for 2 h to ensure equilibrium was reached, then filtered through. The metal ion concentrations in the supernatant were determined by AAS. Metal ions extracted by SSCBB were calculated by the difference. The detection limits, calculated according to this conditions (LOD = 3×SD/slope, $n = 14$), were 0.17, 1.40, and 0.03 mgL^{-1} for Cu, Ni, and Zn, respectively [32]. For the pH adjustment of the aqueous solution NaOH was added.

The extraction percentage was calculated using the following equation;

$$\% \text{ Extraction} = \frac{C_i - C_e}{C_i} \times 100$$

The adsorbed metal quantity was calculated using the following expression;

$$q_e = \frac{(C_i - C_e)V}{W}$$

The distribution coefficient was calculated as:

$$K_d = \frac{(C_i - C_e)}{C_e} \times \frac{V}{W}$$

where q_e is the fixed quantity of metal ion per gram of SSCBB and K_d is the distribution coefficient. C_i and C_e represent the initial and equilibrium concentration of metal ions in aqueous solution, respectively. V is the volume of solution in mL and W is the weight of SSCBB in grams.

Results and discussion

Sol-gel silica chemically bonded with BTMPP (SSCBB)

The synthesis route of the new solid-phase extractor SSCBB can be summarized in Eqs. 1, 2, and 3.
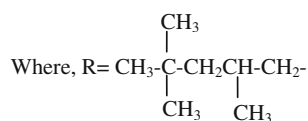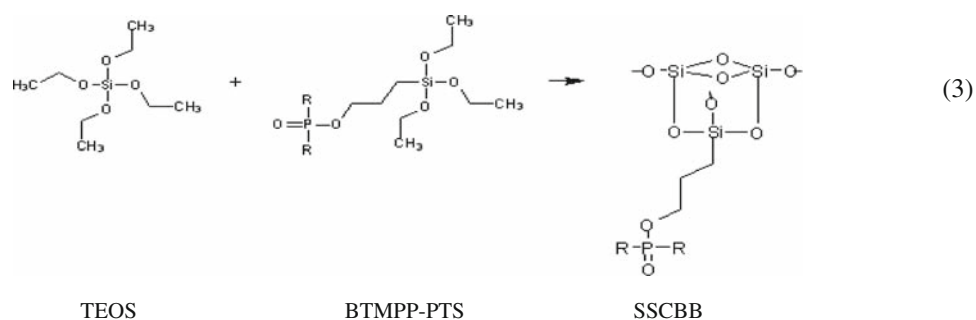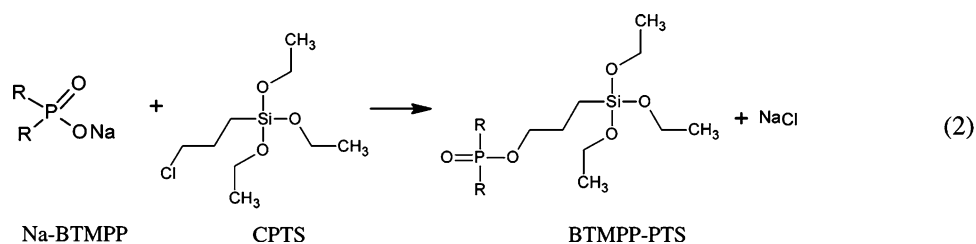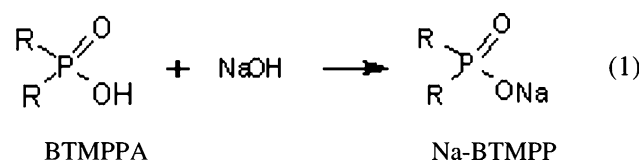
method and the amount was found to be 1.9 mmol of phosphorous per gram of SSCBB.

Physical characterization

Various physico-chemical techniques were used to identify the characteristics of SSCBB since it was newly prepared. BET and BJH method was used to identify the surface state of SSCBB. FTIR spectral analytical method was employed to evaluate the reaction and thermo-gravimetry was used to obtain the thermo-stability of SSCBB.

The SEM images of SSCBB, before extraction and after extraction are shown in Fig. 1. It can be seen from the

The first stage of preparation consisted in reacting sodium hydroxide with BTMPPA to form Na-BTMPP, as shown in Eq. 1. After Na-BTMPP was prepared, reaction of the precursor silylating agent CPTS with a stoichiometric amount of Na-BTMPP yielded the new silylating agent, BTMPP bonded to CPTS, as shown in Eq. 2. Finally the compound BTMPP bonded to CPTS was introduced to TEOS for gelation. The copolymerization occurred due to the silica backbone formation, caused by the basic catalyst. The resulting functionalized material was assigned as SSCBB. The gelation step is illustrated in Eq. 3. The yield obtained of SSCBB was 91.78%. Phosphorous content was determined by ammonium molybdate spectrophotometric

figures that the particle of SSCBB was not homogeneous and after extraction the shape of SSCBB had not changed, indicating SSCBB was stable in aqueous media during extraction. The particle size obtained from particle size analysis was found to be 147.6 ± 57 μm. The BET specific surface area, BJH desorption pore volume and diameter obtained were 21.4 m^2g^{-1}, 0.04 cm^3g^{-1}, and 12.3 nm, respectively. This lower surface area was due to the presence of pendant groups that blocked the access of molecules of gaseous nitrogen into the structure of the anchored silica [33]. The lower surface area and pore volume of SSCBB suggested that a column extraction system was not feasible. Therefore, a batch extraction

Fig. 1 SEM micrographs of SSCBB, before extraction (**a**) and after extraction (**b**)
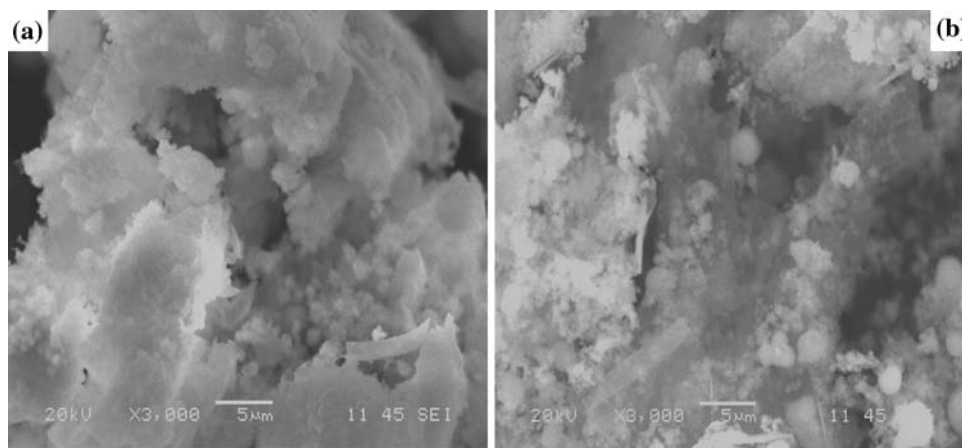
process was applied to remove Cu(II), Ni(II), and Zn(II) from the aqueous solution.

Elemental analysis

The presence of elements in the synthesized solid phase was observed by EDX, which provided the qualitative elemental analysis of the surface of the solid matrix. The elemental analysis of SSCBB, showed for carbon, silicon, oxygen, and phosphorous: 46.78%, 17.3%, 29.55%, and 6.36%, respectively, which confirmed the incorporation of the phosphorous functional group into the silica matrix.

Infrared analysis

The chemical bonding of the phosphorous functional group on the silica matrix was also confirmed by the infrared analysis, as shown in Fig. 2. To understand the bonding of

BTMPP to the silica matrix, a comparison of the FTIR spectrum of the BTMPPA, CPTS, and SSCBB were investigated. For the IR spectra of BTMPPA (Fig. 2b), the bands in the region of 2,700–2,550, 1,160, and 1,048 cm^{-1} were due to the aggregative P–OH vibration, $P = O$ stretching, and P–O–H stretching, respectively [34]. In the IR spectrum of CPTS (Fig. 2c), the band at 850–550, 1,300–1,250, and 2,904 cm^{-1} were assigned to C–Cl band, CH$_2$ wagging mode of CH$_2$Cl and C–H stretching, respectively [35, 36]. In the spectra of SSCBB (Fig. 2a), the bands due to aggregative P–OH vibrations of BTMPP in the region of 2,700–2,550 cm^{-1}, the wagging mode of CH$_2$Cl and C–Cl band of CPTS in the range of 1,300–1,250 and 850–550 cm^{-1} were found to be absent. These findings suggest that at the time of SSCBB preparation, hydrogen was replaced with sodium (Eq. 1) and chlorine was displaced with sodium (Eq. 2). The absence of the P–O–H band, the C–Cl band and CH$_2$Cl wagging mode,

**Fig. 2** IR spectra of SSCBB (a), BTMPPA (b), and CPTS (c)
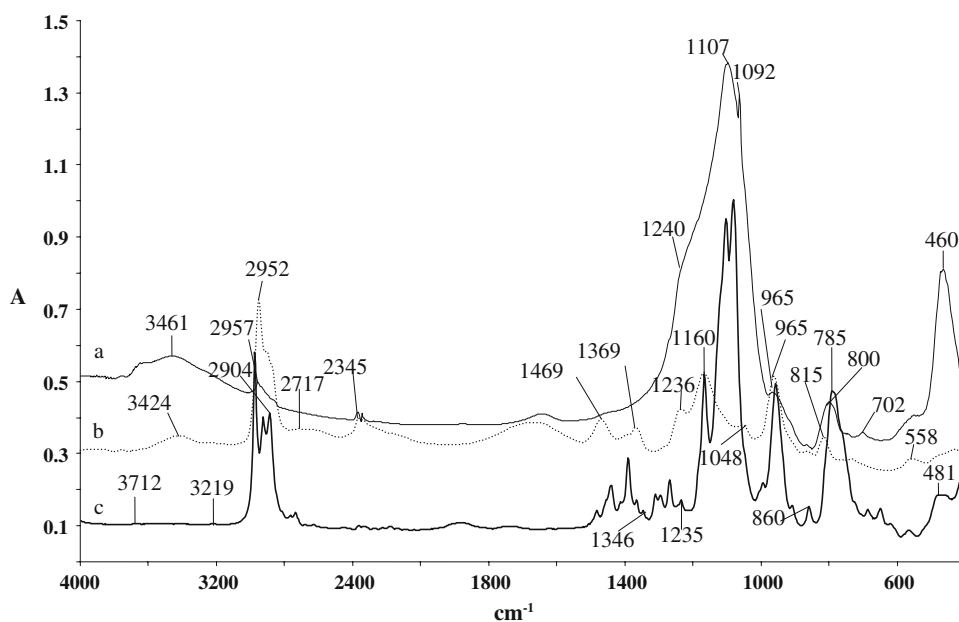
and the presence of $P = O$ and P–C bonded stretching at 1,107 cm^{-1} and 800 cm^{-1}, which was shifted from 1,160 cm^{-1} to 1,107 cm^{-1} for $P = O$ bond [34] and 815 cm^{-1} to 800 cm^{-1} for the P–C bond [36], and the presence of C–H stretching at 2,952 cm^{-1} and the C–C band at 1,240 cm^{-1} [36], certainly suggest the chemical bonding of BTMPP with CPTS. Moreover, the spectrum of SSCBB presented the band at 1,092, 965, and 460 which assigned to the asymmetric stretching of Si–O–Si, Si–OH, and Si–O–Si bending [37], respectively, agrees with the copolymerization of the silica backbone.

Thermal analysis

The TG-DTA and DSC curves for blank silica and SSCBB are shown in Fig. 3. The first mass loss for blank silica below 100 °C in TG curve was attributed for the loss of adsorbed water and ethanol on the silica surface, which corresponds to an endothermic peak; both in the DTA and DSC curve around 60 °C and 160 °C, respectively. For SSCBB, it was found to have an endothermic peak in the DTA curve around 200 °C for the release of adsorbed water and ethanol corresponding to an endothermic peak at 100 °C in the DSC curve. The mass loss from 230 to 770 °C in the TG curve, presented by several DTA peaks at 320–420 °C and 680–770 °C for the decomposition of the several organic groups and the phosphorous functional group of BTMPP in SSCBB, respectively, correspond to an endothermic peak at 320–420 °C in the DSC curve. However, the decomposition of physically immobilized Cyanex 272 into sol-gel silica was obtained at a temperature level from 330 to 580 °C [17], while the decomposition of functional group of SSCBB occurred at 680–770 °C, attributed that SSCBB is more thermally stable than physically immobilized Cyanex 272.

Fig. 3 DSC curve (**a**) and TG-DTA curves (**b**), [A and B for TG curve, and C and D for DTA curve of SSBCC and blank silica, respectively]
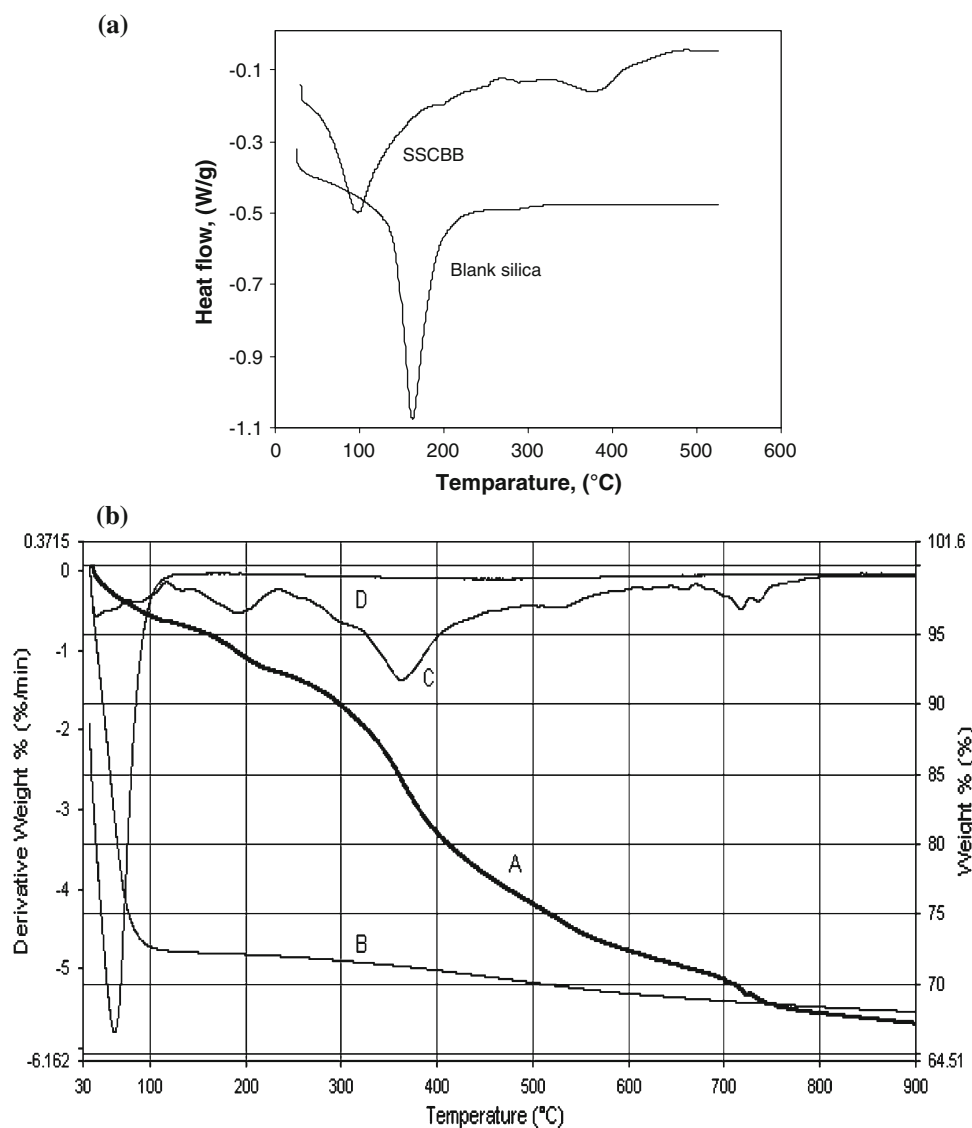
Extraction studies

Effect of contact time

To determine the optimum contact time for the extraction of metal ions with SSCBB, extraction capacity of metal ions was studied as a function of equilibration time. Figure 4 shows the effect of equilibration time on the percentage of extraction for metal ions. It can be seen from the figure that the percentage of extraction increased rapidly up to 30 min for all metals. Equilibrium time was attained within 60 min because increasing the contact time more than 60 min had no significant effect on the extraction of metal ions. So 60 min for the extraction time was adopted for subsequent studies.

Effect of equilibrium pH

The effect of equilibrium pH on the extraction percentage of metal ions is shown in Fig. 5. A general increase in extraction with increasing pH of the solution was observed. For Zn(II) extraction, almost 100% extraction was obtained at a pH of 4.0, for Cu(II) and Ni(II) that of a pH of 6.0 and 8.8, respectively. At a low pH, the competition between metal ions and the higher concentration of H^+ ions at extraction sites favored H^+, and as a result, a smaller percentage of extraction was observed with a low pH. As the pH increased the electrostatic attraction between the metal ions and solid surface increased, as a result, the percentage of extraction also increased [21]. A pH $_{1/2}$ value
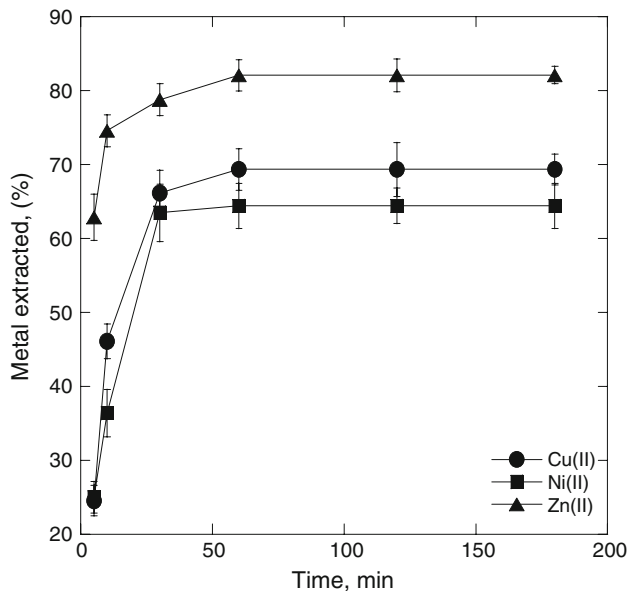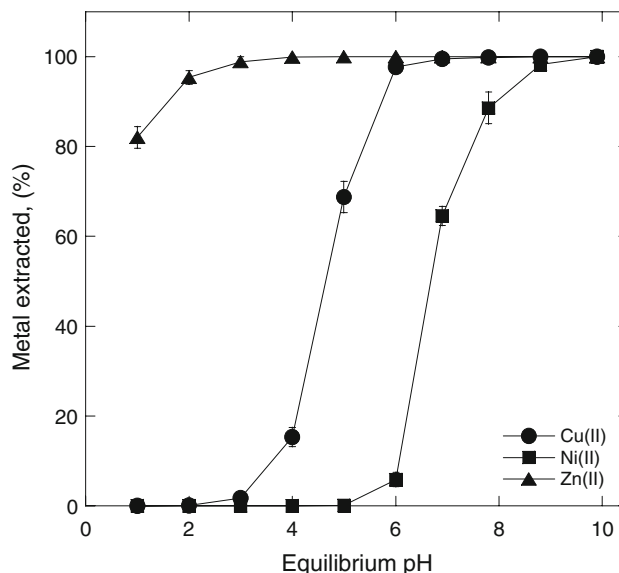

Fig. 5 Effect of equilibrium pH on percentage extraction of metal ions, solid/liquid = 0.02 gL^{-1}, $[Cu(II)]_{ini}$ = 1.57 $mmolL^{-1}$; $[Ni(II)]_{ini}$ = 0.34 $mmolL^{-1}$ and $[Zn(II)]_{ini}$ = 0.31 $mmolL^{-1}$
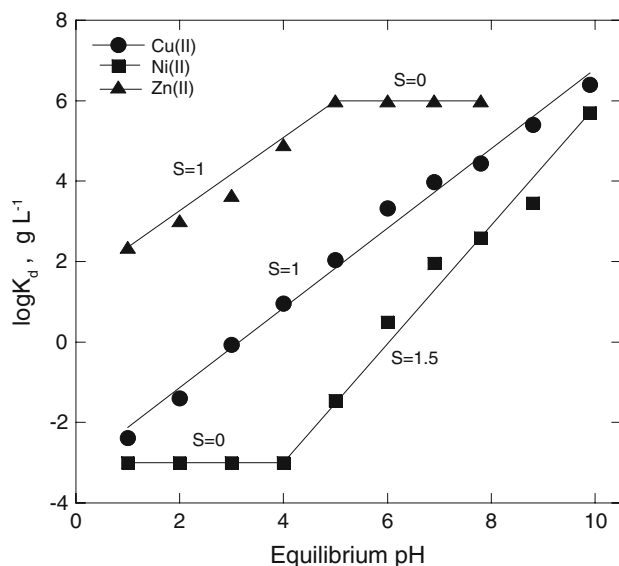
is the value of pH where 50% extraction occurred. The pH $_{1/2}$ values were less than 1 for Zn(II), 4.6 and 6.6 for Cu(II) and Ni(II) extraction, indicating the possible selective removal of these metals by SSCBB.

The distribution coefficient that was calculated and plotted against the equilibrium pH is shown in Fig. 6. The slope value was 1 at the lower pH region (1.0–5.0) for Zn(II) extraction and whole pH region (1.0–9.9) for Cu(II) extraction, indicating that one mole of metal ion was competing with one mole of H^+. For Ni(II) extraction, the slope value was 1.5 at the higher pH region (4.0–9.9), indicating the mixed extraction mechanism had occurred.
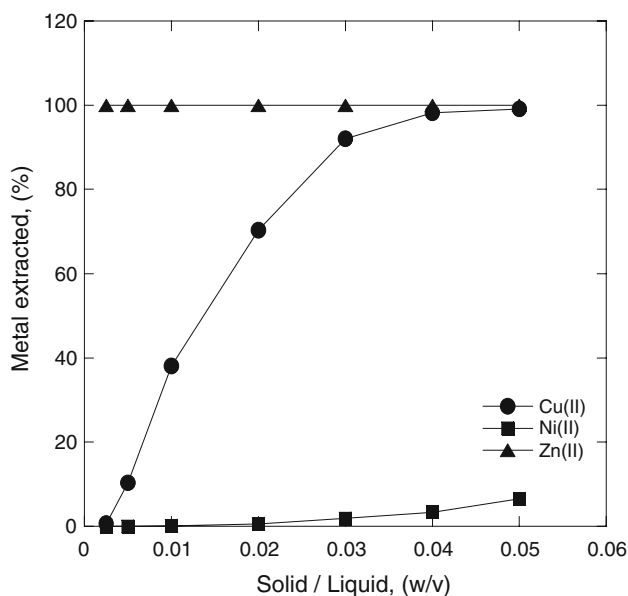
Effect of solid to liquid ratio and BTMPP

The effect of solid (SSCBB) to liquid (aqueous solution) ratio was studied varying the weight of SSCBB from 0.025 g to 0.5 g using a constant volume of aqueous solution of 10 mL. Effect of solid/liquid ratio (w/v) on the extraction of metal ions was investigated in the range of 0.0025–0.05 gL^{-1}, as shown in Fig. 7. The results showed that extraction of Cu(II) increased with the increasing solid to liquid ratio up to 0.04 gL^{-1} after that it became level. There was no significant effect of the solid to liquid ratio on the extraction of Zn(II) in the range studied. The extraction of Ni(II) was nil using the ratio of 0.0025 gL^{-1} and the extraction level increased very slowly as the ratio increased. However, selective removal of Ni(II) from the Cu(II) and Zn(II) solution could be possible by using a solid to liquid ratio of 0.0025 gL^{-1} at a pH of 5.0.

The effect of solid to liquid ratio on extraction was studied and the corresponding BTMPP concentration in

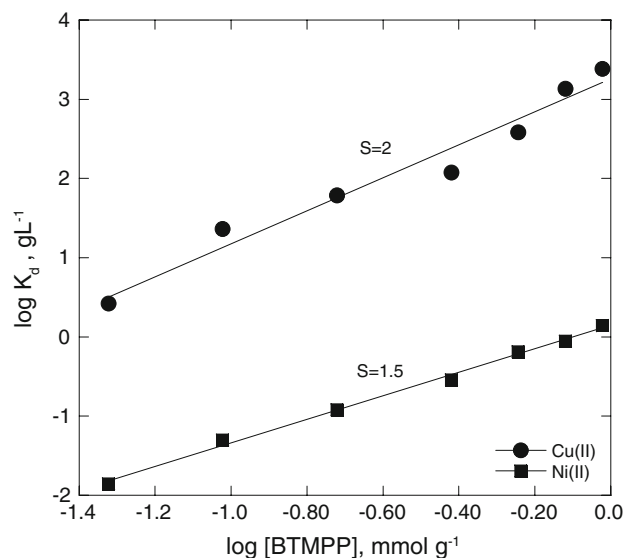**Fig. 4** Effect of contact time on percentage extraction of metal ions, solid/liquid = 0.02 gL^{-1}, $[Cu(II)]_{ini}$ = 1.57 $mmolL^{-1}$, pH = 5.0; $[Ni(II)]_{ini}$ = 0.34 $mmolL^{-1}$, pH = 7.0 and $[Zn(II)]_{ini}$ = 0.31 $mmolL^{-1}$, pH = 1.0

Fig. 6 Effect of equilibrium pH on distribution coefficient, solid/liquid = 0.02 gL^{-1}, [Cu(II)]$_{ini}$ = 1.57 mmolL^{-1}; [Ni(II)]$_{ini}$ = 0.34 mmolL^{-1} and [Zn(II)]$_{ini}$ = 0.31 mmolL^{-1}

Fig. 8 Effect of BTMPP concentration on distribution coefficient. pH = 5.0, [Cu(II)]$_{ini}$ = 1.57 mmolL^{-1}; [Ni(II)]$_{ini}$ = 0.34 mmolL^{-1} and [Zn(II)]$_{ini}$ = 0.31 mmolL^{-1}

Ni(BTMPP)$_2$ species were formed for Cu(II) and Ni(II) extraction during the extraction process.
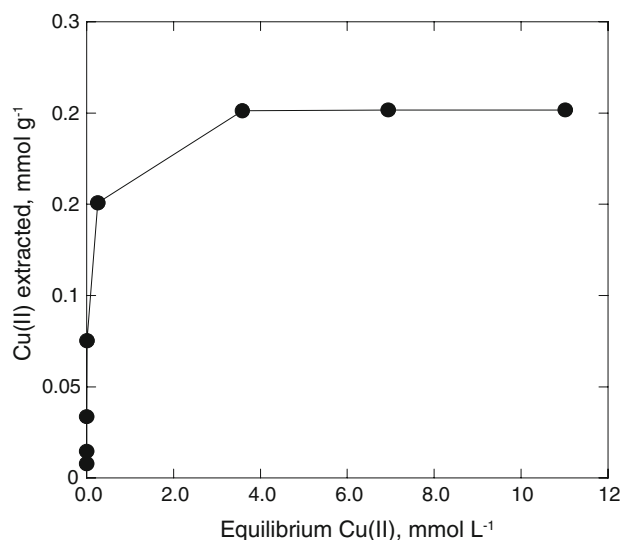
Effect of initial copper ion concentration

The extraction of Cu(II) as a function of Cu(II) in equilibrium with the extracted Cu(II) on 1 g SSCBB was plotted, and the obtained result is presented in Fig. 9. The figure showed that the maximum extraction capacity of SSCBB was 0.2 mmolg^{-1}. In other research, polystyrene microcapsules coated with Cyanex 272, gave a maximum loading capacity of MC-Xs by Cu(II) of 0.055 mmolg^{-1} [38], sol-gel silica immobilized with Cyanex 272 had the adsorption capacity of Cu(II) 0.32 mmolg^{-1} of solid [17], and the sorption capacity of silica gel functionalized with resacetophenone was 0.186 mmol of Cu (II) g^{-1} of the solid phase [39].

Stripping study

The effect of sulfuric acid concentration on the stripping of Cu(II) from the loaded SSCBB was studied in the range of 1–5 molL^{-1} H$_2$SO$_4$. Optimum percentage stripping was obtained using 3 molL^{-1} H$_2$SO$_4$. Stripping occurred with acidic solution because the coordination bond between Cu(II) ions and the functional group of SSCBB was disrupted and then Cu(II) ions were released into the aqueous media.

Regeneration and reuse

To make the solid phase economically competitive, the solid phase should have reusability. The uptake performance of

Fig. 7 Plot of percentage extraction versus solid/liquid ratio, pH = 5.0, [Cu(II)]$_{ini}$ = 1.57 mmolL^{-1}; [Ni(II)]$_{ini}$ = 0.34 mmolL^{-1} and [Zn(II)]$_{ini}$ = 0.31 mmolL^{-1}

solid was calculated and plotted against the distribution coefficient as shown in Fig. 8. The results showed that the distribution coefficient increased with an increasing BTMPP concentration in the solid phase. The slope values of 2 for Cu(II) and 1.5 for Ni(II) extraction indicated two moles of BTMPP, and mixing of one mole and two moles of BTMPP was involved in Cu(II) and Ni(II) extraction reaction. From the slope values, it could be concluded that Cu(BTMPP)$_2$, and mixing of Ni(BTMPP)(Ac/SO$_4$) and

Fig. 9 Adsorption isotherm of Cu(II) on SSCBB at pH = 6.0, Initial, $[Cu (II)]_{ini} = 0.19$, 0.36, 0.84, 1.89, 4.03, 8.62, 11.98, and 16.05 mmolL^{-1}

Fig. 10 Proposed flow sheet for the removal of Cu(II), Ni(II), and Zn(II)

SSCBB after ten (10) use-regeneration cycles shows no sign of degradation. The chemical bonding of BTMPP with silica makes SSCBB stable in regeneration. However, in the case of physical immobilization, meager amounts of Cyanex 272 had been leached out in the aqueous phase for each cycle, as a consequence the uptake performance decreased gradually with the increasing of cycles [17].

Removal of Cu(II), Ni(II), and Zn(II) using SSCBB

Based on the results of this experiment, separation or removal of Cu(II), Ni(II), and Zn(II) would be possible from the aqueous waste from industrial or household sources containing the Cu(II), Ni(II), and Zn(II) concentrations close to the experiment studied. A proposed flow sheet for the separation or removal of Cu(II), Ni(II), and Zn(II) by SSCBB is shown in Fig. 10. Metal solutions are first subjected to Zn(II) extraction at a pH of 5.0 with a solid to liquid ratio of 0.0025 g mL^{-1}. Then the loaded SSCBB is stripped with H$_2$SO$_4$, which gives a Cu(II)- and Ni(II)-free ZnSO$_4$ solution. Subsequently Zn(II) free raffinate was used for Cu(II) extraction at a pH of 5.0 with a solid to liquid ratio of 0.02 gmL^{-1} in five stages and after stripping the loaded SSCBB with H$_2$SO$_4$, Zn(II)- and Ni(II)-free CuSO$_4$ solution was obtained. Finally, Cu(II) and Zn(II) free raffinate was used for Ni(II) extraction at a pH of 9.0 with a solid to liquid ratio of 0.01 gmL^{-1}. So, using this flow sheet, it would be possible to separate Cu(II), Ni(II), and Zn(II) successfully from their mixture. Cyanex 272 is a well-known extractant which can extract
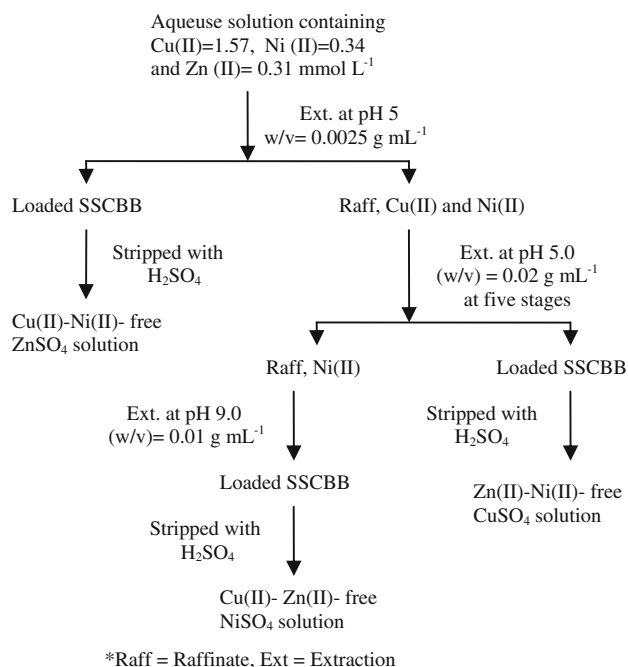
wide range of metal ions such as Cu(II), Ni(II), Zn(II), Fe(III), Co(II), Mg(II), Al(III), Ln(III), etc. [28, 29, 34, 36, 38]. Since SSCBB contains anion of Cyanex 272, it would be useful for those metals which can be extracted by Cyanex 272.

Conclusion

The results demonstrated that the chemical bonding of BTMPP into a silica matrix was successful in forming a new stable support. The new material, containing a phosphorous functional group, had great ability to extract Cu(II), Ni(II), and Zn(II) from aqueous solutions. Equilibration time was found to be 60 min for all metals. Extraction was dependent on the pH of the aqueous phase, the solid to liquid ratio and the initial Cu(II) concentration. It had a capacity of 0.2 mmol of Cu(II) per gram of SSCBB. It can be regenerated and reused repeatedly more than ten times. Easy preparation of SSCBB, cost-effectiveness, the absence of organic solvents in extraction, good reusability and high thermal stability make this solid phase attractive for the removal of Cu(II), Ni(II), and Zn(II) from its aqueous media.

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