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Synthesis and Surface Modification of Mesoporous Silicate SBA-15 for the Adsorption of Metal Ions

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Abstract: In this study surface modified SBA-15, coated with octadecyltrichlorosilane (C18), is considered as an alternative adsorbent for metal ions in water. The SBA-C18 was loaded with Bis(2,4,4-trimethylpentyl) phosphinic acid (cyanex 272) as the metal ion extractant. The adsorption characteristics of phosphinic acid loaded SBA-C18 were evaluated for Cu(II) and Zn(II) ions in aqueous solution. Adsorption tests indicated that a contact time of 1 hour was sufficient for adsorption equilibrium to occur. The $pH_{1/2}$ values of Zn(II) and Cu(II) onto SBA-C18, were found to be similar to published data for levextrel ion exchange resins and around 1 pH unit lower than published solvent extraction data for cyanex 272 in xylene.

Keywords: SBA-15, mesoporous silicate, adsorption, metal ions, surface modification

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INTRODUCTION

Since the discovery of MCM-41 in 1992, there has been much interest and research into mesoporous silicate materials. There are examples of the use of MCM-41 in catalysis, development of gas adsorption theory, and separation of large biological molecules (1, 2), however these examples are limited and further work needs to be done to develop the industrial applications of mesoporous silicates. The greatest advantage of these materials is their large surface area, uniform pore size, and controlled surface chemistry and hence their potential for adsorption processes. This study examines the potential of SBA-15 as a new support for ion exchange and adsorption systems.

There are several aims in the further development of novel ion exchangers and adsorbents. The first is the use of ion exchangers as a replacement for traditional solvent extraction systems. Solvent extraction requires large volumes of potentially toxic organic solvents. An ion exchange material with the ability to selectively and repeatedly adsorb and desorb metals could potentially replace certain solvent extraction processes, hence removing the need to use organic solvents. Another aim is to develop adsorbents with high selectivity for certain metals. Strongly metals-selective adsorbents are useful for a number of industries, including metals recovery and analytical applications.

The results of studies of the adsorption of transition metals onto MCM-41 have been presented in previous papers (3, 4). These studies examined the comparative adsorption behavior for Cu, Cd, and Pb at various pH values, using acetylacetone (Hacac) as a chelating agent. The results showed that the MCM-41/Hacac system has potential as an ion selective adsorbent material. However, MCM-41 is known to become unstable and break down in water over a period of time (4). This is due to its highly hydrophilic surface characteristics. Breakdown of MCM-41 can be prevented by addition of a hydrophobic surface coating. One example is a coating of long chain hydrocarbon molecules attached to the surface of the MCM-41, with a functional group that interacts with the metal ion reagent in the aqueous phase (5).

The problem with surface coating of MCM-41 is that its large surface area is due to its pore characteristics. The typical measured pore diameter for MCM-41 is of the order of 3 nm (4), large enough for acetylacetone-metal complexes but not for some larger chelating molecules such as Bis (2,4,4-trimethylpentyl) phosphinic acid (cyanex 272). It is important that the hydrocarbon molecule used is long enough to create a suitable hydrophobic surface, but not so large that the pores are essentially filled by the coating, preventing diffusion of metal chelates into the pores.

One solution to this problem is to use SBA-15, a newer mesoporous silicate material. SBA-15 is a highly ordered material possessing a regular two dimensional hexagonal array of channels. It is similar in structure to the better known MCM-41, however due to its larger pore size and thicker pore walls it has the ability to capture larger molecules and chemical complexes and has greater stability in aqueous solution (6). This material typically has a pore diameter of the order of 7–10 nm, more than twice that of MCM-41 (7).

In this study SBA-15 is synthesized and coated with octadecyltrichlorosilane (C18) by contacting the mesoporous silicate with a mixture of dehydrated toluene and C18 for 24 hours under reflux. The surface modified SBA-15 is loaded with a chelating agent and assessed for its potential as a highly metals selective adsorbent material for industrial and analytical laboratory applications. The industrial extractant, cyanex 272, has been selected as the chelating agent in this study. Cyanex 272 is used commercially for the extraction of nickel and cobalt from ores, has a high selectivity for several transition metal ions and is well described in the literature (8). This investigation is an example of how one of a family of phosphorous-based extractants can be used in conjunction with a mesoporous silicate to produce a novel way to adsorb metals from aqueous solutions.

EXPERIMENTAL

Synthesis

SBA-15 was synthesized using a triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (pluronic P123, molecular weight = 5800, EO20PO70EO20, Aldrich) as a templating agent. In a typical preparation, 8.0 g pluronic P123 was added to 60.0 g water and stirred at 35°C for 4 hours until the pluronic was dissolved completely. 240.0 g of 2 mol L^{-1} HCl was added and stirred for 2 hours at 35°C. Finally 17.0 g of Tetraethoxysilane (TEOS, Aldrich) was added to the solution and stirred at 35°C for 20 hours. The precipitated mixture was then aged at 100°C for 24 hours in a sealed Teflon vessel. The silicate product was washed with 1 litre of hot water, filtered and dried overnight under vacuum. The material was calcined in a muffle furnace to remove the surfactant, by increasing the temperature by 1°C min^{-1} to 550°C and heating at that temperature for 4 hours under flowing air (7).

Surface Modification

8.0 g of calcined SBA-15 was mixed with 200 mL of dehydrated toluene and 40.0 g of n-octadecyltrichlorosilane (C18, Aldrich) for 24 hours at 150°C under reflux. The suspension was then washed with 120 mL methanol for 3 hours at 100°C. The suspension was cooled to room temperature, washed several times with toluene and methanol, and filtered on a millipore filtration apparatus. The SBA-C18 was then dried at room temperature under vacuum overnight (9).

Loading SBA-C18 with Cyanex 272

Industrial grade cyanex 272 was purified using the procedure specified by Komatsu and Freiser (1989) (10). 5.0 g of SBA-C18 was contacted with 20 mL of a 1:1 mixture of purified cyanex 272 and toluene in a screw capped bottle at 4°C for 24 hours. The cyanex 272 loaded SBA-C18 was washed with distilled water and filtered on a millipore apparatus. The filtered SBA-C18 was then dried at room temperature under vacuum overnight.

Characterization of Synthesized Materials

The nitrogen adsorption and desorption isotherms for calcined and surfaced modified SBA-15 samples were measured at −196°C on a Belsorp 18 (BEL Japan Ltd). Calcined samples were heated at 200°C for 2 hours and degassed overnight, whilst surface modified samples were heated at 150°C for 2 hours and degassed overnight, prior to adsorption. Specific surface areas were determined from the linear section of a BET plot. Pore diameter and pore volume were determined from N_2 desorption data using the Dollimore-Heal (DH) method (11).

The C18 surface coating was analysed by Infrared spectroscopy using a Jasco FT/IR 680. The infrared spectra of calcined and SBA-C18 were analysed and compared using the IR searchmaster^{TM} software package. The acid loading of the SBA-C18 was determined via an oxygen flask combustion method (12). The combustion products were dissolved in a dilute hydrogen peroxide solution and the amount of phosphate in solution measured by HPLC. The mass of phosphorous in the solid sample is calculated, which can then be used to determine the cyanex 272 loading on the SBA-C18.

Adsorption Experiments

The adsorption experiments were conducted by contacting 0.1 g of cyanex 272 loaded SBA-C18 with an aqueous solution containing $1.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ M(II) nitrate (copper or zinc) and $2.0 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$ buffer (acetic acid or chloroacetic acid). The ionic strength was adjusted to $0.1\,\mathrm{mol\,L^{-1}}$ by adding sodium perchlorate and the pH of samples were adjusted using perchloric acid and sodium hydroxide. The samples were agitated for periods of between 1 and 48 hours at 25°C. After the reaction was complete the samples were centrifuged and filtered. The aqueous solutions were analysed for metals concentration by ICP-AES. The pH of the samples were measured both before and after the adsorption test and it was noted that there was usually some drop in pH after adsorption.

RESULTS AND DISCUSSION

Characterization Experiments

The mesoporous silicate samples were analysed using gas adsorption analysis with liquid nitrogen. The surface areas of normal SBA-15 samples were almost all in the range of 800 to 900 $m^2 g^{-1}$. The adsorption/desorption isotherms for SBA-15 and SBA-C18 are shown in Fig. 1. The plots show a type IV isotherm, with a distinctive stepped shape, typical of mesoporous materials with one-dimensional cylindrical channels (7). There are three distinct regions in the adsorption isotherms (See Fig. 1), indicating monolayer adsorption (P/Po up to 0.7), capillary condensation (around 0.7 to 0.78) and multilayer adsorption (above 0.78). The capillary condensation step of the adsorption/desorption isotherm for SBA-C18 is shifted to a lower P/Po value than for normal SBA-15. This indicates smaller pores due to the C18 surface coating. This result is confirmed by the smaller pore diameter and pore volume results given in Table 1. Based upon the surface area and pore size results presented in Table 1, the surface modified SBA shows a 20% reduction in pore diameter, however there is a greater reduction in surface area. This may be due to blockage of some of the pores with excess C18, which may not have been completely removed during the washing step of the surface modification procedure.

The infrared spectra of normal and surface modified SBA are shown in Fig. 2. The infrared spectrum of SBA-C18 is largely influenced by the underlying silicate surface, whilst the C18 coating produces lower transmittance values and new peaks in the infrared spectrum at higher wave numbers.

Cortina and coworkers (13) have studied a levextrel ion exchange resin (produced by Bayer AG), which contains di(2,4,4-trimethylpentyl) phosphinic

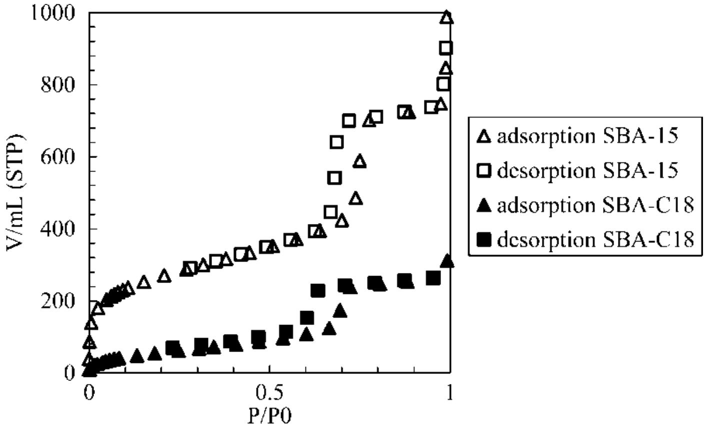

Figure 1. Nitrogen adsorption and desorption isotherms of normal and surface modified SBA-15.

Table 1. Material characteristics of normal and surface modified SBA-15. Pore diameter and Pore volume calculated by the BDH-method (Dollimore and Heal, 1964) (11)

	Specific surface area (BET) $m^2 g^{-1}$	Pore diameter nm	Pore volume $cm^3 g^{-1}$
SBA-15	862 (±36)	8.54	1.11
SBA-C18	275 (±79)	6.93	0.74

acid as the active extractant. The total acid loading of the levextrel resin was determined by elution of the ligand using ethanol, followed by titration with NaOH. The levextrel resin was found to have 1.09 mol of phosphinic acid per kilogram dry resin (13). In this study, after loading the chelating reagent onto the SBA-C18, the amount of cyanex 272 retained was determined via the oxygen flask combustion method (12). The combustion products were dissolved in MilliQ water and a small amount of hydrogen peroxide and analysed by HPLC. Based upon the mass of sample combusted and the concentration of phosphate found in the aqueous sample, the amount of phosphinic acid was found to be 2.43 mol kg^{-1} SBA-C18. This is more than twice the amount of extractant determined for the levextrel ion exchange resin. For the adsorption tests 0.1 g of SBA-C18 was contacted with 10 mL of aqueous solution. Hence there is around 1.42×10^{-2} mol L^{-1} chelating reagent available to participate in the adsorption reaction.

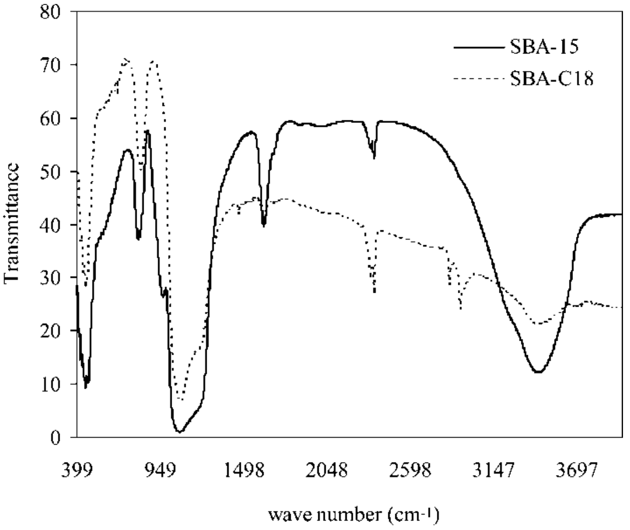

Figure 2. Infrared spectrum of normal and surface modified SBA-15.

Adsorption Experiments

Initially the effect of reaction time on adsorption equilibrium was tested to determine the optimum time for subsequent experiments. Cyanex 272 loaded SBA-C18 (0.1 g) was contacted with aqueous solution containing 1×10^{-4} mol L^{-1} Zn(II) for periods between 1 and 48 hours (See Fig. 3). Figure 3 shows no significant change in adsorption with increasing contact time, indicating that a period of 1 hour is sufficient for adsorption equilibrium. Previous investigators have looked at the stability of normal SBA-15 in acidic and neutral aqueous solutions. It has been found that SBA-15 is very stable in weakly acidic solutions (pH 3.72) and will only undergo minor ($<15\%$) degradation in pH 6 solutions after a period of 21 days (7). In this investigation the SBA-15 has been modified with a hydrocarbon surface coating, which essentially makes the material hydrophobic.

The adsorption behavior of two transition metals, Zn^{2+} and Cu^{2+}, onto cyanex 272 loaded SBA-C18 was investigated with respect to pH of the aqueous phase (Fig. 4). The SBA-C18 was contacted with an aqueous solution containing 1×10^{-4} mol L^{-1} metal ions, 2×10^{-2} mol L^{-1} buffer and pH adjusted using perchloric acid or sodium hydroxide. Figure 4 shows that the SBA-C18 adsorption is more favorable for zinc than for copper, which is as expected based on the chemistry of cyanex 272. Zinc is adsorbed onto SBA-C18 above pH 2 with maximum adsorption occurring above pH 3.5, whereas copper is adsorbed above pH 3.2 with maximum adsorption above pH 5.

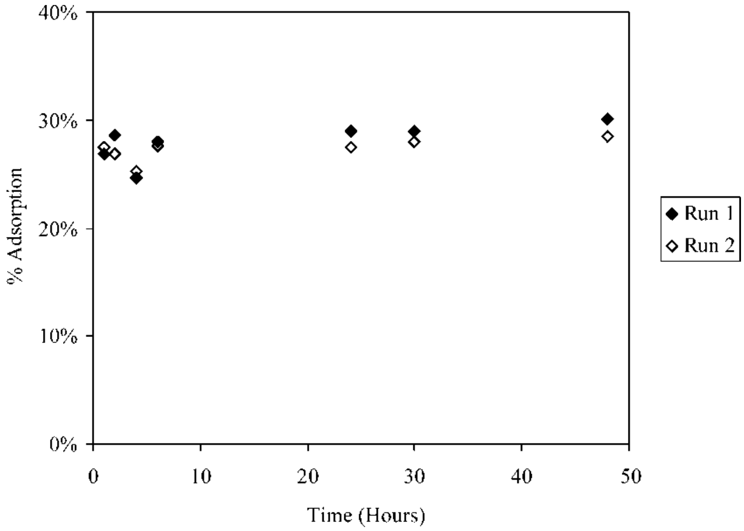

Figure 3. The effect of contact time on the adsorption of Zn(II) onto SBA-C18. Zinc concentration 1×10^{-4} mol L^{-1}, pH 2.27.

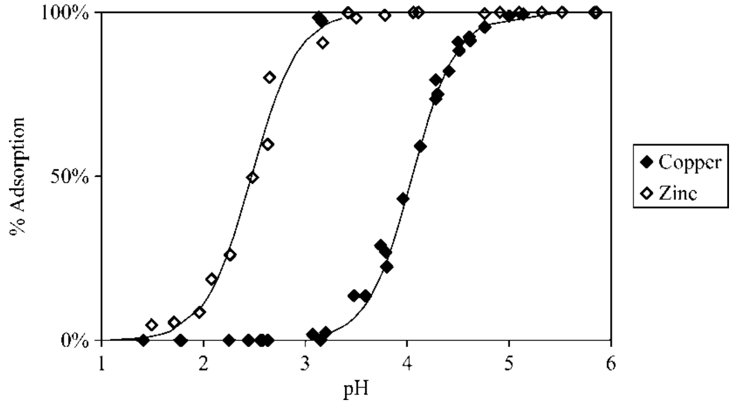

Figure 4. Adsorption of Zn^{2+} and Cu^{2+} onto cyanex 272 loaded SBA-C18, as a function of pH. The solid lines indicate the metal/cyanex extraction isotherm, with copper and zinc equilibrium constants of 3.98×10^{-5} and 6.3×10^{-2} respectively.

The reaction equation for the adsorption of divalent metal ions onto SBA-C18 can be described as follows:

$$M^{2+} + 2HR_{(SBA-C18)} \Leftrightarrow MR_{2(SBA-C18)} + 2H^{+} \quad (1)$$

where M represents the metal species and R represents the cyanex 272 loaded onto the SBA-C18. The equilibrium coefficient, K_{eq}, for copper and zinc adsorbed onto SBA-C18 is defined as:

$$K_{eq} = \frac{[MR_2][H^+]^2}{[M^{2+}][HR]^2} \quad (2)$$

Equation 2 was used to calculate and plot the extraction isotherms shown in Fig. 4. The K_{eq} values for copper and zinc were calculated as 3.98×10^{-5} and 6.3×10^{-2} respectively.

The distribution coefficient, K_d, is denoted as:

$$K_d = [M]_{solid}/[M]_{aqueous} \quad (3)$$

where $[M]_{solid}$ and $[M]_{aqueous}$ are the metal concentrations in the solid phase ($mol\,g^{-1}$) and aqueous phase ($mol\,cm^{-3}$). The plots of distribution coefficient with respect to pH are shown in Fig. 5. A straight line with slope +2 can be plotted through the data, indicating that the adsorption reaction is described well by equation 1.

Table 2 compares the pH values for 50% adsorption of copper and zinc onto SBA-C18 ($pH_{1/2}$), to two other methods of metals adsorption/extraction. The first method is solvent extraction using cyanex 272 as the extractant and xylene as the organic phase (8). The second method is ion exchange using levextrel resin (13). The published value for copper in the cyanex

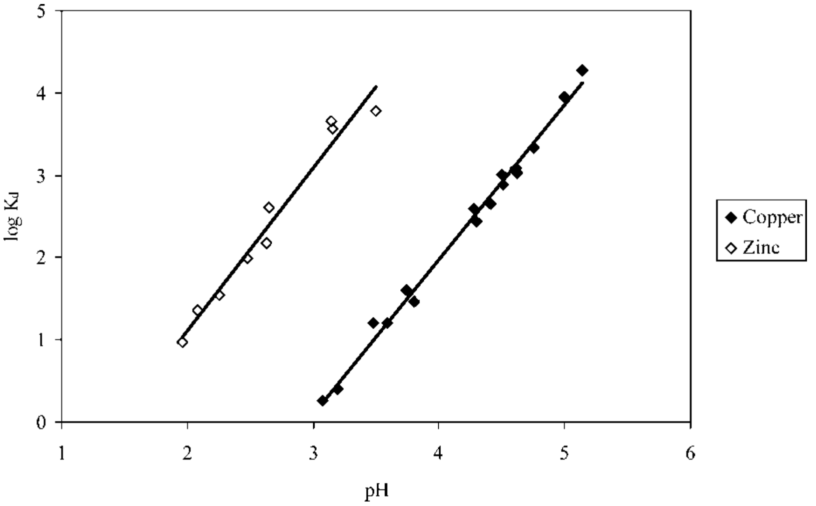

Figure 5. Distribution coefficient of divalent transition metal ions on SBA-C18. The slope of the lines are +2.

272/xylene solvent extraction system is 5.0, compared to a value of 4.0 for the SBA-C18 experiments. The levextrel resin has a $pH_{1/2}$ value of 3.7 for copper, which compares well with the SBA-C18 results. Published data for the solvent extraction system and ion exchange system gives the $pH_{1/2}$ value for zinc as 3.4 (8), and 2.3 respectively (13). The extraction experiments for the solvent extraction system were carried out with an aqueous phase ionic strength five times greater than that of the SBA-C18 or the levextrel resin systems (See Table 2). Increased ionic strength has been found to shift extraction equilibria to higher pH values, (8) which would explain the difference in the $pH_{1/2}$ results reported for the solvent extraction system. This is confirmed by the similar pH results at the same ionic strength for the SBA-C18 and levextrel resin systems. These results indicate that the cyanex 272 loaded SBA-C18

Table 2. Comparison of $pH_{1/2}$ values for divalent metal ion adsorption onto SBA-C18, ion exchange and solvent extraction using cyanex 272 in xylene

Adsorption/extraction method	$pH_{1/2}$ Copper	$pH_{1/2}$ Zinc
Cyanex 272 on SBA-C18	4.0	2.5
[a]Solvent extraction using phosphinic acid in xylene	5.0	3.4
[b]Levextrel resin containing phosphinic acid	3.7	2.3

[a] Data from Sole and Hiskey (1992) (8). Cyanex 272 concentration 0.05 mol L^{-1}, ionic strength 0.5 mol L^{-1} as Na_2SO_4.

[b] Data from Cortina et al (1996) (13). Ionic strength 0.1 mol L^{-1} as $NaNO_3$.

system, similar to the ion exchange resin system, is well suited to the adsorption of transition metal ions from aqueous solutions.

A comparison of zinc adsorption using cyanex 272 loaded SBA-C18, with solvent extraction using Na-cyanex 272 in kerosene, is shown in Table 3. In the SBA-C18 experiments; a $98.2\,\mathrm{mg\,L^{-1}}$ zinc solution, contacted with 0.1 g of SBA-C18 at pH 2.7, adsorbed $7.23\,\mathrm{mg\,Zn^{2+}}$ per gram of SBA-C18. This is equivalent to 73.6% adsorption of zinc from solution and 15.4% of cyanex-272 is used in the reaction. For the solvent extraction using Na-cyanex in kerosene (14), a $0.08\,\mathrm{mol\,L^{-1}}$ solution of zinc was contacted with a kerosene organic phase containing $0.1\,\mathrm{mol\,L^{-1}}$ Na-cyanex 272. The solvent extraction system adsorbed 62.9% of Zn from the aqueous phase and 6.1% of cyanex 272 participated in the reaction. Based upon these results, the adsorption of zinc onto SBA-C18 is shown to be good for low metal loadings, where organic loss is a problem in solvent extraction. The pH of 2.7, used in this test is not the optimum value for zinc adsorption onto SBA-C18. It is thought that at a pH of 3.5 or more, the loading capacity of zinc onto SBA-C18 will be even higher and there will be a larger proportion of cyanex 272 which will participate in the reaction.

CONCLUSIONS

This study looks at the adsorption characteristics of surface modified SBA-15, produced by surface coating the mesoporous silicate with octadecyltrichlorosilane (C18). The metal chelating reagent used was purified cyanex 272, which was loaded onto the synthesized SBA-C18. The amount of cyanex 272 on the SBA-C18 was found to be $2.43\,\mathrm{mol\,kg^{-1}}$ SBA-C18, more than twice the phosphinic acid loading capacity of a levextrel ion exchange resin. The cyanex 272 loaded SBA-C18 was contacted with Cu(II) and Zn(II) ions in aqueous solution. Adsorption tests over intervals of between 1 and 48 hours showed that the reaction occurred quickly and that a contact time of 1 hour was sufficient for adsorption equilibrium to occur. It was found that cyanex 272 loaded SBA-C18 had a high adsorption capacity of 7.23 mg Zn(II)/g

Table 3. Comparative data for removal of zinc from aqueous solution

System	Cyanex concentration (M)	Zn^{2+} adsorption/extraction	% Zinc removal	% Cyanex used
Cyanex 272 on SBA-C18	0.04	$7.23\,\mathrm{mg\,Zn\,g^{-1}}$ SBA	73.6	15.4
[a]Na-cyanex in kerosene	0.1	$2\,\mathrm{mg\,Zn\,cm^{-3}}$ organic	62.9	6.1

[a]Data from Devi et al (1997) (14).

SBA at pH 2.7 and high utilization of cyanex 272 in the reaction compared to published solvent extraction studies. The $pH_{1/2}$ values of Zn(II) and Cu(II) onto SBA-C18 of 2.5 and 4.0 respectively occur at a lower pH than published solvent extraction data for cyanex 272 in xylene, but are similar to published pH values for a levextrel resin containing di(2,4,4-trimethylpentyl) phosphinic acid. Overall the results of this investigation have shown the cyanex 272/SBA-C18 system has strong metals selectivity, high extractability and hence good potential as an alternative to established solvent extraction systems.

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