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Rinez Thapa: Conceptualization, Methodology, Investigation, Writing - Original Draft, Visualization, Funding acquisition

Tuomo Nissinen: Conceptualization, Methodology, Writing - Review & Editing

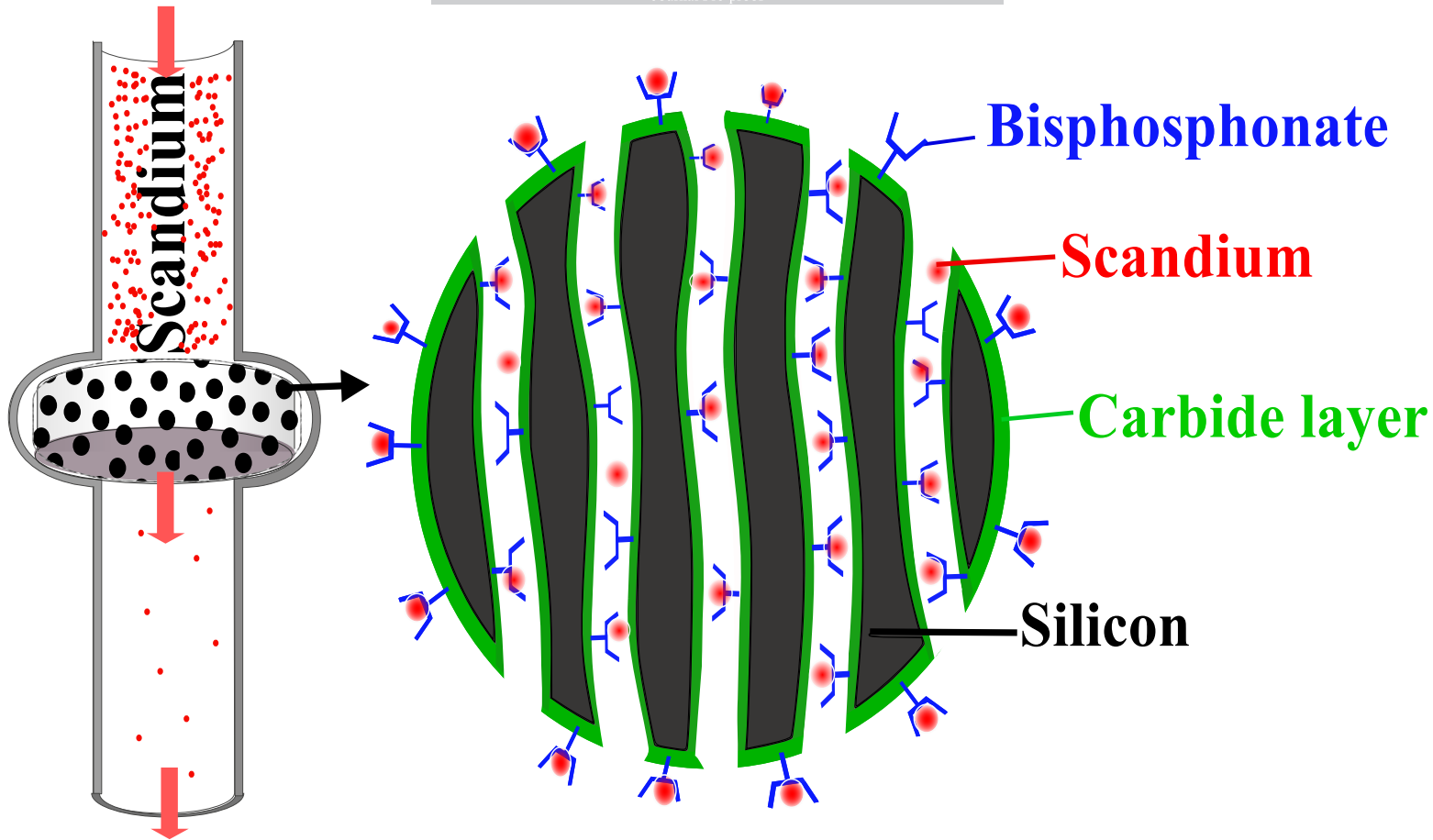
Petri Turhanen: Resources

Juha Määttä: Methodology, Investigation, Resources

Jouko Vepsäläinen: Resources

Vesa-Pekka Lehto: Conceptualization, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition

Joakim Riikonen: Conceptualization, Methodology, Writing - Review & Editing, Supervision, Project administration, Funding acquisition



Bisphosphonate modified mesoporous silicon for scandium adsorption

Rinez Thapa^a, Tuomo Nissinen^a, Petri Turhanen^b, Juha Määttä^c, Jouko Vepsäläinen^b, Vesa-Pekka Lehto^{a*} and Joakim Riikonen^a.

^aDepartment of Applied Physics and ^bSchool of Pharmacy, University of Eastern Finland, P.O.Box 1627, Yliopistonranta 1, FI-70211 Kuopio, Finland.

^cBioMediTech, Faculty of Medicine and Health Technology, Tampere University and Tampere University Hospital, Arvo-Ylpön katu 34, FI-33520 Tampere, Finland.

*Corresponding Author: Email: vesa-pekka.lehto@uef.fi

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Abstract

Scandium has several applications in advanced technology, but its wider utilization is restricted by the limited supply. Scandium exists in low concentration in ores and therefore the conventional extraction methods are difficult, uneconomical, and often hazardous to the environment. Adsorption technology is more sustainable method to extract scandium, because of low energy consumption and scalability. However, selectivity and stability of adsorbents are often inadequate. The present paper introduces a novel hybrid material as a robust adsorbent for efficient extraction of scandium. The material comprises of bisphosphonate molecules grafted on thermally carbonized surfaces of mesoporous silicon. The mesoporous framework was utilized to make the material water permeable to use in a flow-through system, and the surface modifications made the material exceptionally stable even in harsh conditions. The material exhibited a remarkable selectivity towards scandium with a separation factor of 13, which is 3-fold higher compared with the commercial ion

exchange resin Dowex 50WX8. Crucially, the hybrid material proved to be highly stable and reusable up to 50 adsorption/desorption cycles of scandium.

Keywords: scandium; adsorption; mesoporous; silicon; bisphosphonates; selectivity.

1. Introduction

Scandium (Sc) is used in the development of high-tech materials for various applications. It is mainly used as an effective alloying element (0.2 – 0.6 wt. % Sc) with aluminum making it stronger, lighter and more resistant to corrosion. The Sc-Al alloys are used in aerospace industry, transportation and sports equipment [1]. Utilization of Sc is growing in solid oxide fuel cells because of high oxygen ion conductivity of Sc₂O₃-stabilized-ZrO₂ solid electrolytes even at low temperatures [2]. Recently, Sc has been used to enhance the piezoelectric response in aluminum nitride alloys [3]. Other applications are in ceramics, high intensity metal halide lamps and lasers [4].

Regardless of the numerous applications, extensive use of Sc has not been feasible due to its scarcity and high price [4]. Sc is expensive, because its purification is very difficult and time consuming. Exploitable ores of Sc (e.g. thortveitite) are rare; however, Sc often co-exists in ores of other minerals but in low concentrations [5]. Exploitation of these ores containing traces of Sc is not economically viable. Therefore, Sc is usually produced as a by-product from the mine tailings such as uranium-leached liquors, titanium pigment production wastewaters, tungsten refinery and bauxite residues [6].

Conventional hydrometallurgical processes used in the recovery, like precipitation and solvent extraction, have major drawbacks. The precipitation method yields poor Sc purity due to co-precipitation of other metals present in large quantities [5,6]. Solvent extraction is mainly operated in large-scale and requires treatments with a large volume of hazardous organic solvents, which leads to potential toxic emissions into the environment [7]. The

methods are also not economically convenient for the low Sc contents due to the high acid consumption as well as the complications associated with reusing the extractant.

As a greener alternative, adsorption technology has the potential to extract Sc more efficiently in terms of simplicity and low operating cost. To be a feasible adsorbent, the material must repeatedly and selectively adsorb and desorb Sc ions without any essential loss in the performance. Commercially available adsorbents such as ion-exchange resins suffer from fouling problems as well as swelling of its polymeric structure during adsorption/desorption processes, which eventually leads to deterioration of the material [8,9]. To overcome these issues, hybrid materials consisting of metal binding molecules on a rigid framework is a promising technique. Particularly, mesoporous silica has been widely used, because of their high surface areas offering high degree of functionalization [10]. However, the stability of the silica-based material is limited because of the dissolution of the pore walls leading to poor reusability [10,11]. Indeed, the reusability of the hybrid materials are rarely reported for more than 10 cycles [12-18].

The adsorption technology can be simplified using a flow-through setup to adsorb/desorb metals in a continuous process. The hybrid materials can be conveniently packed in a column where the metal solution flows through swiftly due to the high permeability facilitated by the porosity of the material. In terms of the reusability, not only the mesoporous framework but also the functional molecules and the linkage between them must be stable to sustain the durability of the hybrid material. Bisphosphonates consisting $O=P-C-P=O$ structure are stable molecules that have been demonstrated to collect several metal cations from mining process waters [19].

In our earlier research, bisphosphonate molecules with terminal alkene were directly grafted on thermally carbonized surfaces of mesoporous silicon. The synthesized material showed exceptional stability in highly acidic/basic solutions [20]. Herein, we investigate the

adsorption mechanisms alongside the selectivity of the adsorbent towards Sc. Furthermore, we demonstrate the capability of the material to operate in a flow-through system to extract scandium efficiently over 50 adsorption/desorption cycles. The obtained results were compared with the commercial ion exchange resin Dowex 50WX8 frequently used for Sc extraction in the literature [21,22].

2. Experimental section

2.1 Materials, chemicals and standard solutions

Hydrofluoric acid (HF 38–40 %, Merck), ethanol (EtOH 99.5 %, Altia Oy) and silicon wafers (Okmetic Oyj) were used for preparation of porous silicon (PSi). Bisphosphonate molecule (*Tetrakis(trimethylsilyl) 1-(trimethylsilyloxy) undec-10-ene-1, 1-diylbisphosphonate*) was synthesized and characterized as reported elsewhere [20]. Mesitylene (99 % extra pure, ACROS OrganicsTM) was purchased from Fisher Scientific, Finland. Standard solution of Sc³⁺ (1000 mg/L in 1 wt % HNO₃, AAS standard) and the ion-exchange resin, Dowex 50WX8; hydrogen form, 100 – 200 mesh (Dow Chemical companyTM) were purchased from Sigma-Aldrich, Finland. The resin is a strong cation exchanger containing sulfonic acid (SO₃H) functional groups. Metal standards (1000 mg/L) of AlCl₃, FeCl₃, CuCl₂ and ZnCl₂ were all Titrisol standards purchased from Merck KGaA, Germany. Milli-Q water was used throughout the experiments.

2.2 Synthesis of porous silicon (PSi). Silicon wafers with resistivity of 0.01–0.02 Ωcm were electrochemically etched in 1:1 HF/EtOH mixture applying current density of 30 mA/cm² for 40 min. PSi films were detached from the wafers with lift-off current pulses of 160 mA/cm² (1 sec) and 255 mA/cm² (2 sec) with 1 sec pause between the pulses. The films were then dried for 1 h at 65 °C. The dry PSi films were first hand ground into coarse particles and later milled (100 rpm, 3 mins) in a planetary ball mill (Fritsch Pulverisette 7). The particles were then sieved into 25–75 μm size fraction.

2.3 Thermal carbonization of PSi. The PSi microparticles were immersed in 1:1 HF/EtOH solution for 10 min and the sample was dried for 45 min at 65 °C. The dry PSi powder was transferred into a quartz tube and flushed with N₂ at 1 L/min for 30 min. The nitrogen flow was maintained throughout the treatment. Acetylene gas at 1 L/min was added first for 15 min at room temperature (RT). Then the tube was inserted into a preheated tube oven and heated at 500 °C for 14 min 30 sec. Then acetylene flow was ended and after 30 sec at 500 °C, the quartz tube was taken out from the tube oven and the sample was cooled at RT for 30 min. At the room temperature, the acetylene flow was resumed for 9 min 40 sec. After 20 sec, the sample was inserted into the tube oven at 820 °C for 10 minutes. The manufactured thermally carbonized particles (TCPSi) were cooled at RT for 40 min under N₂ atmosphere.

2.4 Synthesis of BP-TCPSi. The BP molecule was conjugated on TCPSi particles by mixing 1:2 mass ratio of BP:TCPSi under N₂ atmosphere without exposing the TCPSi to air after the thermal carbonization. Before the mixing, BP was first degassed in 10 ml of mesitylene solution by bubbling with N₂ gas for 20 min. The BP solution was transferred into the quartz tube and mixed with the TCPSi particles. The quartz tube was sealed with a Teflon stopper and the sample was incubated at 120 °C under N₂ atmosphere. After 19 h, the unbound BP molecules and the mesitylene was removed by washing the particles with 200 mL MeOH in suction filtration (polypropylene PP, 10 µm pore size) and dried at 65 °C for 1 h. A reference TCPSi sample was prepared identically except no BP was added into the mesitylene.

2.5 Material characterization and instrumentation

The median particle size of TCPSi and BP-TCPSi samples was measured with Mastersizer device (Mastersizer 2000, Malvern Instruments, UK) using EtOH as dispersant. The surface area, pore volume and pore diameter of the particles were determined from N₂ adsorption/desorption isotherms (Micromeritics Tristar II 3020). Prior to the measurement, samples were degassed at +65 °C in vacuum (VacPrep 061, Micromeritics) for 1 h.

The amount of BP grafted on TCPSi was measured with thermogravimetric analysis (TGA Q50, TA instruments). The samples were first equilibrated at 80 °C for 30 min and then heated to 700 °C at the rate of 20 °C/min under nitrogen flow (120 mL/min), and the mass loss was measured as a function of temperature. The BP content (% w/w) from BP-TCPSi sample was calculated by comparing the mass loss between BP-TCPSi and unfunctionalized TCPSi sample.

Samples for scanning electron microscope (SEM, Zeiss Sigma HP VD) coupled with energy dispersive X-ray spectroscopy (EDS, ThermoScientific) were prepared by cluing the microparticles on a standard aluminium stub with conducting carbon adhesive. Acceleration voltage was 5.0 kV and the images were recorded with SE2 or InLens Detector. The acceleration voltage was increased to 15.0 kV for EDS analysis.

2.6 Adsorption studies

2.6.1 Batch setup

The adsorbents were first primed by mixing in acidic media for 1h; the TCPSi or the BP-TCPSi particles were primed with 10 ml of 5 M HCl whereas the Dowex 50WX8 resin was primed with 10 ml of 0.125 M H₂SO₄ (as instructed by the manufacturer), and both adsorbents were washed three times with 10 mL Milli-Q water to obtain neutral pH. The pH of Sc solution at desired concentration was adjusted with HNO₃ or NaOH. Adsorption experiments were conducted in 15 mL centrifuge tubes by mixing the desired amount of the adsorbent with 10 mL Sc solution in an orbital shaker at 80 rpm for the pre-determined times. Subsequently, adsorbent was separated from the suspension by centrifugation (6000 rpm, 1 min) and the supernatant aliquot was measured by inductively coupled plasma mass spectrometer, ICPMS (NexION 350D, Perkin Elmer). The adsorbed metal amounts (Q_e in $\mu\text{mol/g}$) was calculated using following equation.

$$Q_e = \frac{(C_o - C_e)V}{m} \times \frac{1000}{MW} \quad (1)$$

Where, C_0 and C_e are the metal concentration (mg/L) before and after the adsorption respectively, m is the mass of adsorbent (mg) and V is the volume of metal solution (mL) whereas MW represents the molecular weight of the metal ion (g/mol).

2.6.2 Flow-through setup

Lab-scale flow-through setup (supplementary material, Figure S1) consisted of a syringe pump (AL-1600, New Era Pump Systems Inc.), 30 mL plastic syringes and glass columns (Omnifit[®] Labware, 2.5 cm × 0.3 cm, volume 0.2 mL). Mass of 20 mg of either the BP-TCPSi particles or the Dowex 50WX8 resin were packed inside the column on a polypropylene (PP) sheet with 10 μm pores. Unlike the BP-TCPSi that was free flowing, it was not possible to pour the Dowex resin into the column. Therefore, the resin was first mixed with water and then inserted into the column using a syringe. Priming was done by filtering 5 ml of the acidic media mentioned above (in section 2.6.1) applying the flow rate of 0.2 mL/min. After that, adsorbents were washed with 10 mL water at 1 mL/min. Adsorption step was carried out by filtering 5 mL of the metal solution at 0.25 mL/min, whereas desorption was performed with 15 mL of 1 M HNO₃ at 1.25 mL/min. After every adsorption and desorption step, adsorbent was washed with water as described above. Duration for a complete cycle was 52 min. Desorbed metal amount (D_a in μmol/g) was calculated using following equation.

$$D_a = \frac{C_{des} \times V}{m} \times \frac{1000}{MW} \quad (2)$$

Where, C_{des} is the metal concentration of filtrate after desorption step (mg/L).

The flow through setup was employed to examine i) the selectivity of BP-TCPSi and Dowex towards Sc and b) the reusability of BP-TCPSi upto 50 adsorption/desorption cycles. To provide distinct comparison of the Sc selectivity between the adsorbents and pH values, a separation factor (SF) was calculated using following equation.

$$SF = \frac{C_{des(Sc)}}{C_{des(Al+Fe+Cu+Zn)}} \bigg/ \frac{C_{0(Sc)}}{C_{0(Al+Fe+Cu+Zn)}} \quad (3)$$

The calculated SF value quantified how effectively Sc was purified from the metal mixture after a complete adsorption/desorption cycle, which is a crucial measure of the adsorbent's efficacy.

2.6.3 Isotherm titration calorimetry (ITC) analysis

In order to successfully inject the BP-TCPSi into ITC cell, the particles were ground in a mortar and sieved into $\leq 10 \mu\text{m}$ size fraction. Priming was done in above mentioned acidic media (see section 2.6.1) but intense centrifugation (4000 rpm, 20 min) was used to separate the particle suspension. The particles were re-dispersed in pH water (pH 1 or pH 3) and degassed prior to the measurements. The BP-TCPSi suspensions; 0.9 – 1.14 mM concentration of bisphosphonates at pH1 and 0.57 – 1.0 mM at pH3 were placed into the ITC cell under constant 440 rpm stirring and titrated with 4.0 mM Sc. The heat evolved or consumed in each 10 μl injection was measured at 25 °C. Reference measurements buffer-to-buffer, buffer-to-particles and scandium-to-buffer were subtracted from the results. The measurements were conducted on a high-sensitivity VP-ITC (Malvern, Microcal Inc.) and data were analysed in Microcal Origin 7.0 software (MicroCal LLC, Northampton, MA, USA) as described elsewhere [23].

3. Results and discussion

3.1 Characterization of BP-TCPSi

The median particle size of BP-TCPSi was 73.3 μm (particle size distribution shown in Supplementary material, Figure S2). SEM images (Figure 1) revealed an irregular morphology of the microparticles and pore openings on the surface of the BP-TCPSi particles. The N_2 sorption isotherms were of the type IV, showing a hysteresis loop typical for mesoporous structure. The isotherm shape was unchanged after BP functionalization

(Supplementary material, Figure S3). The results from the gas adsorption are summarized in Table 1. The conjugation of BP molecules slightly reduced the pore volume, surface area and pore diameter as expected. The amount of BP grafted on TCPSi was determined from TGA curves (Figure 2) and the mass loss attributed to decomposition of BP was 1.98 ± 0.04 % w/w equivalent to 60 ± 1 μmol BP per gram of the sample. The presence of BP on TCPSi was further confirmed from EDS analysis (Supplementary material, Figure S4), where a phosphorous peak at 2.01 KeV was detected in the spectrum of BP-TCPSi sample but not in TCPSi sample.

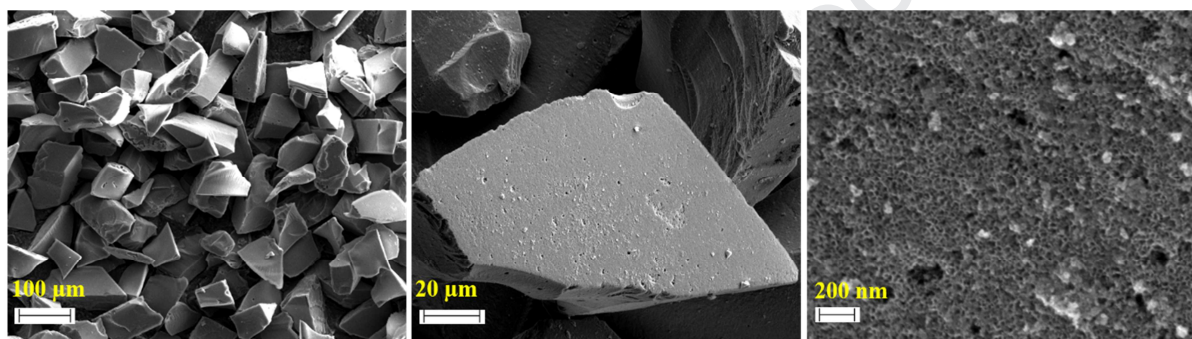


Figure 1. SEM results showing the morphology and porous structure of BP-TCPSi particles.

Table 1. Results from N_2 physisorption of TCPSi and BP-TCPSi samples (mean \pm σ , $n=3$).

Materials	Surface area (m^2/g) ^a	Pore volume (cm^3/g) ^b	Pore diameter (nm) ^c
TCPSi	250 ± 3	0.65 ± 0.01	10.5 ± 0.1
BP-TCPSi	220 ± 2	0.56 ± 0.01	10.1 ± 0.1

^a BET surface area calculated from the isotherm.

^b Specific pore volume calculated from desorption isotherm at $p/p_0 = 0.9$.

^c Average pore diameter calculated by BJH theory using desorption branch of isotherm.

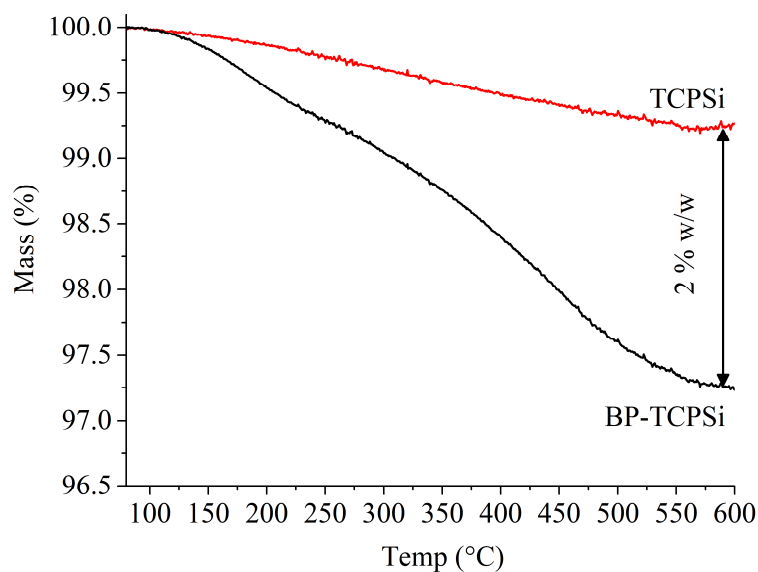


Figure 2. TGA curves of TCPSi and BP-TCPSi samples.

3.2 Adsorption isotherms

The adsorption studies were performed at pH 1 and pH 3. The pH values above 3 were excluded to avoid the risk of Sc precipitation at pH >4 [14,18,24] Deprotonation constant; pKa values of BP molecule (Figure 3) are pKa₁=1.0, pKa₂ = 2.5, pKa₃ = 6.7, pKa₄=10.6 and pKa₅=11.6 [25].

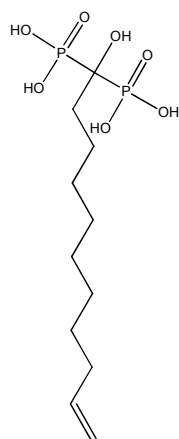


Figure 3. Chemical structure of bisphosphonate molecule grafted on the BP-TCPSi particles.

The studies were started by examining the adsorption kinetics in order to determine the equilibrium time for the adsorption isotherm studies in batch type setup. The equilibrium times for adsorption were determined from the starting points of the plateau in the kinetics

curves (Supplementary material, Figure S5), which were 8 h at pH 1 and 24 h at pH 3. Based on the kinetics, 24 h time was selected for the adsorption isotherm to ensure equilibrium state is achieved.

Adsorption isotherms with BP-TCPSi and Dowex were measured in a batch type setup by varying the adsorbent mass (10 – 100 mg) at constant initial concentration of Sc. When BP-TCPSi was used, the initial Sc concentration was 2.5 mg/L at pH 1 and 4 mg/L at pH 3.

When Dowex was used, the initial Sc concentration was 45 mg/L at pH 1 and 65 mg/L at pH 3. Langmuir equations were fitted to the experimental isotherm datasets (Figure 4), and the parameters from the fittings are listed in Table 2.

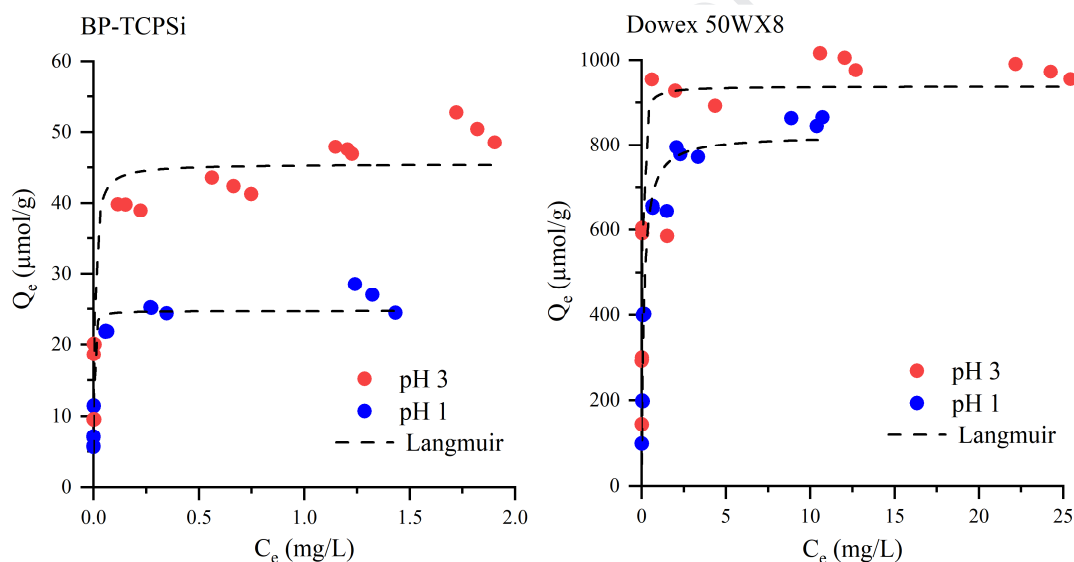


Figure 4. Adsorption isotherms of Sc with BP-TCPSi particles and Dowex 50WX8 resin at pH 1 and pH 3.

Table 2. Results of Langmuir isotherm parameters.

Sample	Q_{\max} ($\mu\text{mol/g}$) ^a	K_L (L/mg) ^b	R^2
BP-TCPSi, pH 1	25 ± 1	780 ± 90	0.95
BP-TCPSi, pH 3	46 ± 2	190 ± 50	0.89
Dowex 50WX8, pH 1	830 ± 30	8 ± 2	0.96
Dowex, 50WX8, pH 3	940 ± 40	50 ± 10	0.91

^a maximum adsorption capacity

^b Langmuir constant

Unfunctionalized TCPSi particles adsorbed a negligible amount of Sc at pH 1 (3.1 ± 1.0 $\mu\text{mol/g}$) and at pH 3 (5.1 ± 1.5 $\mu\text{mol/g}$) (Supplementary material, Figure S6). Since there were no active metal binding sites in TCPSi, the adsorption can be attributed to electrostatic interaction or physisorption, and the experimental data did not fit to the Langmuir model. The Langmuir model fit the isotherms with BP-TCPSi and Dowex 50WX8 with regression coefficient values, $R^2 = 0.9$, indicating that the adsorption follows the Langmuir model in these cases. This means that specific interaction between the metal ion and the phosphonate groups (BP-TCPSi) or sulfonic acid groups (Dowex) are responsible for the adsorption. However, it should be noted that the isotherm for BP-TCPSi at pH 3 showed an increasing trend indicating involvement of another adsorption phenomenon beside the Langmuir model. Maximum capacity (Q_{max}) of BP-TCPSi at pH 1 was half than that at pH 3. The isotherm results can be explained by the proton exchange from the phosphonate groups, where one proton exchange occurs at pH 1 and two at pH 3. Scandium ion can also form coordination bond with P=O group [26,27]. Therefore, chelation occurs by the synergy of the proton exchange mechanism alongside the formation of coordinate bond with P=O [26]. It can be hypothesized that because of a single deprotonation at pH 1 inducing only one anionic O-atom per BP molecule (monodentate ligand), two BP molecules participated in capture of a single Sc cation yielding a low Q_{max} value. At pH 3, a single bidentate BP ligand with two deprotonated O-atoms was enough to chelate one Sc ion.

The type of reaction involved in the binding of Sc with the BP-TCPSi was briefly investigated by ITC analysis (Supplementary material, Figure S7) and the results revealed the exothermic reaction (negative ΔH) at pH 1 but endothermic (positive ΔH) at pH 3. This implies that the binding was enthalpy driven at pH 1 but entropy driven at pH 3. The

exothermic reaction at pH 1 affirmed formation of stronger complexes than in pH 3 between the bisphosphonates and the Sc ions. This result is further supported by the binding affinities given by the Langmuir constant (K_L) values (see Table 2) such that K_L (pH 1) > K_L (pH 3). Nonetheless, the adsorption capacity of BP-TCPSi was considerably lower than the commercial Dowex resin as expected because of the smaller number of functional groups in BP-TCPSi.

For comparison to a previous study [14], Q_{max} of Sc at pH 3 with bare mesoporous silica materials; silica gel, KIT-6 and SBA-15 were 12, 22 and 25 $\mu\text{mol/g}$ respectively despite of very high surface areas (378, 850 and 934 m^2/g). In addition, there was virtually no Sc adsorbed with KIT-6 at lower pH (1.6 – 1.9) due to strong electrostatic repulsion between the metal ion and silica surfaces [14]. The results of present study emphasize the significance of surface modification with suitable metal chelating moieties to complement metal adsorption properties of the mesoporous materials.

3.3 Selectivity

The selectivity experiments were conducted in the flow-through setup using the experimental parameters as described in section 2.6.2. The selectivity studies of BP-TCPSi and Dowex towards Sc were conducted using equimolar solution containing Sc^{3+} , Al^{3+} , Fe^{3+} , Cu^{2+} and Zn^{2+} . When BP-TCPSi was used as the adsorbent, the molar concentration of each metal in the solution was adjusted to 110 μM at pH 1 and 220 μM at pH 3. The corresponding concentrations of Sc^{3+} , Al^{3+} , Fe^{3+} , Cu^{2+} and Zn^{2+} in the solution were 5, 3, 6, 7 and 7 mg/L (pH 1) and 10, 6, 12, 13 and 13 mg/L (pH 3). With the Dowex resin, the molar concentration of each metal was adjusted to 3100 μM at pH 1, in which the corresponding concentrations of Sc^{3+} , Al^{3+} , Fe^{3+} , Cu^{2+} and Zn^{2+} were 140, 85, 175, 200 and 205 mg/L. The results with Dowex resin at pH 3 was unreliable due to high Fe^{3+} concentration leading to precipitation and thus the results were discarded to avoid false interpretation. The selectivity results are

shown in Figure 5. The initial μmol amounts of each metal available for adsorption per gram of the adsorbent (Q_0 in $\mu\text{mol/g}$) were calculated using the equation

$$Q_0 = \frac{c_0 \times V}{m} \times \frac{1000}{MW} \quad (4)$$

The adsorbed/desorbed amounts after the adsorption step (Q_e) and the desorption steps (D_a) were calculated using the equations (1) and (2), respectively.

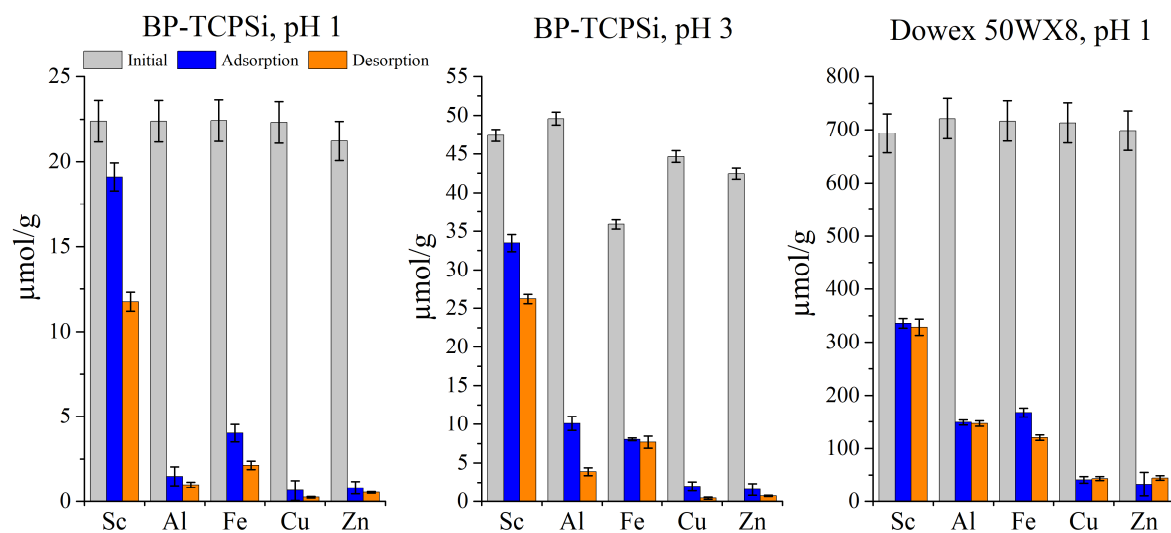


Figure 5. The initial, adsorbed and desorbed amounts of Sc, Al, Fe, Cu and Zn using an equimolar solution with BP-TCPSi at pH 1 and pH 3 and Dowex 50WX8 at pH 1. The results indicate selective adsorption of Sc especially with BP-TCPSi at pH 1. Error bars represent the standard deviation (n=3).

Presented results clearly displayed higher selectivity towards Sc than other metals in the solution, substantially with BP-TCPSi and moderately with Dowex. The selectivity towards Sc with BP-TCPSi was higher at pH 1 ($SF = 13 \pm 1$) than at pH 3 ($SF = 8 \pm 1$), suggesting that the competition of metal ions to occupy the binding sites increases with the increase in solution pH. The total amount of all adsorbed metal ions in BP-TCPSi was $26 \pm 3 \mu\text{mol/g}$ (pH 1) and $55 \pm 3 \mu\text{mol/g}$ (pH 3) whereas in Dowex was $730 \pm 50 \mu\text{mol/g}$ (pH 1). These values reasonably corresponded to the Q_{max} values listed in Table 2. This means that the active binding sites in the adsorbent were fully occupied while unspecific adsorption did not

take place. Based on equation (3), the SF value is directly proportional to the desorption efficiency. It should be noted that the desorption of Sc from the BP-TCPSi particles was not complete, which reduced the SF values.

Generally, adsorption is directly proportional to ionic charge thus; divalent Cu^{2+} and Zn^{2+} were the least efficiently adsorbed. Competitive adsorption of Sc^{3+} with Al^{3+} and Fe^{3+} was expected, as they are all trivalent cations and possess analogous chemical properties in terms of Lewis acidity and atomic size [6,18,24]. The obtained higher selectivity of Sc can be related to its lower hydration enthalpy, (-3897 kJ/mol) than Fe (-4430 kJ/mol) and Al (-4665 kJ/mol) as lesser energy was required for it to dehydrate when occupying the binding sites [17, 28, 29]. Compared with Dowex (SF = 4.3 ± 0.2), BP-TCPSi had 3-fold superior selectivity (SF = 13 ± 1) towards Sc at pH 1. Despite distinctive characteristics between the BP-TCPSi particles and the Dowex resin, the functional moieties (the type of ligand and its denticity) in the adsorbent determine the adsorption properties such that ligands with a larger bite angle favor larger ions while the smaller bite angle favors smaller ions [12, 30]. The O-Sc-O angle in the Sc- PO_4 complexes has a wider range of $63.35 - 104.76^\circ$ than in the Sc- SO_4 complexes of $82.96 - 95.61^\circ$ [29].

3.4 Reusability of BP-TCPSi

Because of the superior Sc selectivity obtained at pH 1, reusability of the BP-TCPSi was investigated using Sc solution (5 mg/L) also at pH 1 for the adsorption. Consecutive 50 adsorption/desorption cycles were completed in the flow-through setup (see section 2.6.2 for experimental parameters) and the results are shown in Figure 6.

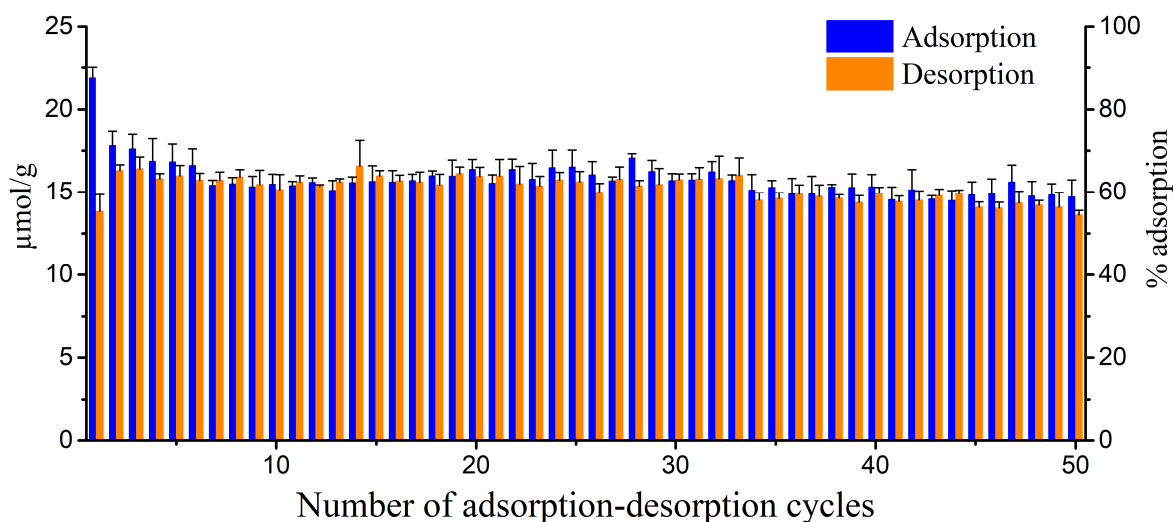


Figure 6. Reusability of BP-PSi for 50 adsorption/desorption cycles of Sc. Error bars represent standard deviation (n=4).

In the 1st cycle, adsorption was 88 ± 3 % of Q_{max} , out of which 21 ± 4 %-units remained in the particles after desorption. It is proclaimed also in literature that because Sc ions are Pearson hard acids, they prefer forming strong complexes with phosphate groups and are therefore difficult to be desorbed by inorganic acids [6, 30, 31]. Nevertheless, the reusability results demonstrated steady adsorption and desorption from the 2nd to 50th cycle in all consecutive cycles; with an average of 60 ± 4 % adsorption and 98 ± 4 % desorption. The leaching of grafted BP molecules from BP-TCPSi during the repeated adsorption desorption cycles was investigated by comparing the amount of BP in the material, measured by TGA, before and after the 50 cycles. The average TGA mass loss of BP-TCPSi measured after the 50 cycles was 2.3 ± 0.6 %. The difference in the mass losses of before and after the 50 cycles was not statistically significant (p-value > α at 0.05) (Supplementary material, Figure S8). The results confirmed that BP molecules were conjugated with exceptional stability in the particles withstanding 50 adsorption/desorption cycles. In addition, there was no compelling difference in the structure and morphology between the untreated BP-TCPSi and cycled BP-TCPSi by visual inspection of SEM images (Supplementary material, Figure S9).

4. Conclusions

Bisphosphonate molecules were directly grafted on the carbonized surfaces of mesoporous silicon (BP-TCPSi). The synthesized adsorbent material was selective towards scandium ions and had excellent stability. An easy-to-use filtration system with the BP-TCPSi particles was demonstrated for the scandium extraction. With a continuous flow of an equimolar metal mixture at pH 1, the BP-TCPSi adsorbent revealed superior selectivity towards scandium compared with a commercial ion exchange resin Dowex 50WX8. BP-TCPSi showed excellent stability and withstood 50 adsorption-desorption cycles without reduction in the performance. The BP-TCPSi adsorbent showed two essential features for a good adsorbent: selectivity and reusability. Hence, the hybrid material together with the filtration system have a great potential to be employed in efficient and environmentally friendly extraction of scandium.

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Tables

Table 1. Results from N₂ physisorption of TCPSi and BP-TCPSi samples (mean \pm σ , $n=3$).

Table 2. Results of Langmuir isotherm parameters.

Figures

Figure 1. SEM results showing the morphology and porous structure of BP-TCPSi particles.

Figure 2. TGA curves of TCPSi and BP-TCPSi samples.

Figure 3. Chemical structure of bisphosphonate molecule grafted on the BP-TCPSi particles.

Figure 4. Adsorption isotherms of Sc with BP-TCPSi particles and Dowex 50WX8 resin at pH 1 and pH 3.

Figure 5. The initial, adsorbed and desorbed amounts of Sc, Al, Fe, Cu and Zn using an equimolar solution with BP-TCPSi at pH 1 and pH 3 and Dowex 50WX8 at pH 1. The results indicate selective adsorption of Sc especially with BP-TCPSi at pH 1. Error bars represent the standard deviation (n=3).

Figure 6. Reusability of BP-PSi for 50 adsorption/desorption cycles of Sc. Error bars represent standard deviation (n=4).

- Mesoporous silicon was functionalized with bisphosphonates for scandium adsorption.
- The material depicted effective selectivity towards scandium.
- The adsorbent was reusable upto 50 adsorption/desorption cycles.

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DECLARATION OF COMPETING INTEREST

We wish to draw the attention of the Editor to the following facts which may be considered as potential conflicts of interest and to significant financial contributions to this work.

The authors Joakim Riikonen, Tuomo Nissinen and Vesa-Pekka Lehto are co-founders and shareholders in a start-up company 3AWater Oy which develops a portable analyzer of metals dissolved in water which uses the kind of material reported in the manuscript. At the time of writing the company has Finnish patent application 20185098 and PCT application PCT/FI2018/050950 which aim to protect the use of the material described in the article in metal adsorption.

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