Electronic Supplementary Information

Novel bisphosphonate-based solid phase method for effective removal of chromium(III) from aqueous solutions and tannery effluents

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Materials and methods

Apparatus

^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer operating at 500.1, 202.5 and 125.8 MHz, respectively. TSP (in D_2O) or TMS (in CD_3OD) were used as internal standards for ^{1}H and ^{13}C measurements, and 85% H_3PO_4 was used as an external standard for ^{31}P measurements. The $^{n}J_{HH}$ and $^{n}J_{HP}$ couplings were calculated from proton spectra, and the $^{n}J_{CP}$ couplings from carbon spectra with the coupling constants given in parenthesis as hertz. ^{13}C and ^{31}P CPMAS NMR measurements of the compounds **2b**, **2c**, **4a**, **4b** were performed with a Bruker AMX-400 FT NMR spectrometer equipped with a magic-angle spinning probehead operating at either 100.61 MHz or 161.97 MHz. Samples were packed in 7 mm ZrO_2 rotors equipped with KEL-F caps and spinning rate was 6 kHz or 4 kHz. CPMAS NMR spectra were measured with a contact time of 5 ms and a delay of 4 s.

Metal concentrations were analyzed either by a Perkin Elmer 5100 atomic absorption spectrometer (AAS) by using air-acetylene flame or by an inductively coupled plasma optical emission spectrometer (ICP-OES). A Thermo Electron iCAP 6600 Duo View equipped with Cetac ASX-520Hs and an autosampler were used. The phosphorus content of synthesized compounds and their solubility in Milli-Q water were determined in a Jasco V-530 spectrophotometer using the modified molybdenum blue method.[1] Solid samples were decomposed with nitric acid by the microwave digestion technique using a CEM MDS-81D

Microwave System prior to phosphorus determination.

Elemental analyses (C, H, N) were accomplished with a ThermoQuest CE Instruments EA 1110-CHNS-O elemental analyzer (CE Instruments, Milan, Italy).

Chemicals

Titrisol standard solutions of $CrCl_3$, $FeCl_3$, $CuCl_2$ and $NiCl_2$ and suprapur HCl and NaOH were supplied by Merck. Diphonix® ion exchange resin (100-200 mesh) was purchased from Eichrom and was used in sodium form. Ultapure Milli-Q water was used throughout the procedures. Valeric acid (99%), nonanoic acid (97%), undecanoic acid (98%), octyl cyanide (98%), 1-bromodecane (98%), 1-bromododecane (97%), 1-bromohexadecane (97%), hydrocinnamic acid (99%), 5-phenylvaleric acid (99%), NaH (60% in oil), benzenesulfonic acid (98%), phosphorus acid (99%), methanesulfonic acid (>99.5%) and phosphorus trichloride (99%) were purchased from Sigma-Aldrich. Caproic acid (98%) and 1-bromoheptane were purchased from Fluka AG. Decanonitrile (98%) was purchased from ABCR and 8-phenyloctanoic acid (97%) from Alfa Aesar. D_2O (99.90% D) and Methanol-D4 (99.80% D) used in the NMR measurements were purchased from Euriso-Top.

Synthesis and identification

Compounds **1a-d, 2a-c, 3a-c** were synthesized according to the general method described by Kieczykowski *et al.*[2] The syntheses of compounds **4a-b, 5a-d** were performed according to methods described previously.[3,4] Though syntheses of compounds **1a-d** have been published earlier[5-8] spectral data of the compounds is missing. Nevertheless, the elemental analysis of **1a-b** was published by Martin *et al.*[5] Syntheses and identification data of the compounds **3a-3c** were previously published by Alanne *et al.*[9] In addition, compounds **4b**, **5a** and **5b** have been described before by Roth *et al.*,[10] but there was no characterization data of the compounds.

The synthesized compounds were crystallized in varying pHs and their composition as acid as well as mono-, di- or 1.5-fold sodium salt was clarified with the elemental analysis. The estimated purity for all compounds was ≥ 98% according to the NMR data, compounds **2c**, **4a** and **5b** being an exception. In the ^1H spectrum of **2c** there were some traces of the starting material (8-phenyloctanoic acid) observed but there were no other phosphorus containing compounds according to the ^{31}P spectrum. Because of the very low solubility of **2c** the exact purity was very difficult to determine based on the NMR data. In the NMR spectra of compounds **4a** and **5b** there were no impurities detected. Nevertheless, the elemental analysis

did not correspond well enough with the calculated values. In the case of **5b**, this was most probably due to minor chlorine traces in the compound since in the last step of the synthesis the isopropyl protecting groups were removed by refluxing in HCl. Since **2c**, **4a** and **5b** did not turn out to be very effective in metal recovery experiments, they were not purified further.

(1-Hydroxypentane-1,1-diyl)bisphosphonic acid **1a**: Valeric acid (2.00 g, 19.58 mmol), phosphorus acid (1.61 g, 19.58 mmol) and methanesulfonic acid (10 ml) were heated to 65 °C with stirring in a flask with a reflux condenser and a $CaCl_2$-tube. PCl_3 (3.43 ml, 39.20 mmol) was added dropwise and the mixture maintained at 65-70 °C for 24 h. Water (30 ml) was added to the cooled mixture and the solution refluxed for 5 h. The product was solidified after pH adjustment to approx. 5 with NaOH (6 M) as monosodium salt and the crude product recrystallized from EtOH-H_2O (1:1.3) yielding 3.21 g (61%) of **1a** as a white solid. ^{1}H NMR (D_2O): δ 2.00-1.88 (2H, m), 1.60-1.51 (2H, m), 1.38-1.29 (2H, m), 0.94-0.88 (3H, m); ^{13}C NMR (D_2O): 77.2 (t, $^1J_{CP}$ = 134.3 Hz), 36.3, 28.7 (t, $^2J_{CP}$ = 6.1 Hz), 25.9, 16.2; ^{31}P NMR (D_2O): δ 18.68 (s). IR (KBr) 2961, 2875, 1468, 1178, 1061, 924 cm^{-1} (OH-stretch very wide, peak not detective around 3000-3500 cm^{-1}).

(1-Hydroxyhexane-1,1-diyl)bisphosphonic acid **1b**: Prepared as **1a** from caproic acid (2.00 g, 17.22 mmol) to give 3.23 g (72%) of **1b**. ^{1}H NMR (D_2O): δ 1.99-1.87 (2H, m), 1.62-1.52 (2H, m), 1.39-1.25 (4H, m), 0.92-0.83 (3H, m); ^{13}C NMR (D_2O): 77.2 (t, $^1J_{CP}$ = 134.9 Hz), 36.6, 35.0, 26.2 (t, $^2J_{CP}$ = 5.9 Hz), 24.8, 16.3; ^{31}P NMR (D_2O): δ 18.68 (s). IR (KBr) 2957, 2873, 1467, 1177, 1061, 928 cm^{-1}.

(1-Hydroxynonane-1,1-diyl)bisphosphonic acid **1c**: Prepared as **1a** from nonanoic acid (1.00 g, 6.23 mmol) to give 1.66 g (77%) of **1c**. ^{1}H NMR (D_2O + 1 drop of 6M NaOD): δ 1.92-1.80 (2H, m), 1.60-1.48 (2H, m), 1.37-1.21 (10H, m), 0.92-0.83 (3H, m); ^{13}C NMR (D_2O + 1 drop of 6M NaOD): 79.6 (t, $^1J_{CP}$ = 131.9 Hz), 39.1, 34.0, 33.3, 31.9, 31.6, 27.2 (m), 24.8, 16.3; ^{31}P NMR (D_2O + 1 drop of 6M NaOD): δ 19.36 (s). IR (KBr) 2926, 2855, 1467, 1177, 1062, 926 cm^{-1}. Anal. Calcd. for $C_9H_{20}Na_2O_7P_2$: C, 31.05; H, 5.79; P, 17.8. Found: C, 31.55; H, 5.97; P, 17.6.

(1-Hydroxyundecane-1,1-diyl)bisphosphonic acid **1d**: Prepared as **1a** from undecanoic acid (3.00 g, 16.10 mmol) to give 4.35 g (74%) of **1d**. ^{1}H NMR (D_2O + 1 drop of 6M NaOD): δ 2.00-1.87 (2H, m), 1.61-1.52 (2H, m), 1.38-1.21 (14H, m), 0.90-0.83 (3H, m); ^{13}C NMR (D_2O + 1 drop of 6M NaOD): 40.5 (t, $^1J_{CP}$ = 103.7 Hz), 39.2, 34.0, 33.3, 32.0, 31.9, 31.6, 31.3, 27.2 (m), 24.8, 16.2; ^{31}P NMR (D_2O + 1 drop of 6M NaOD): δ 18.77 (s). IR (KBr) 2924, 2853, 1469, 1178, 1062, 933 cm^{-1}. Anal. Calcd. for $C_{11}H_{24.5}Na_{1.5}O_7P_2$: C, 36.17; H,

6.76; P, 17.0. Found: C, 36.35; H, 6.43; P, 17.2.

(1-Hydroxy-3-phenylpropane-1,1-diyl)bisphosphonic acid **2a**: Prepared as **1a** from hydrocinnamic acid (2.42 g, 16.12 mmol) to give 1.70 g (31%) of **2a**. ^{1}H NMR (D_2O): δ 7.43-7.36 (4H, m), 7.31-7.25 (1H, m), 2.98-2.91 (2H, m), 2.28-2.18 (2H, m); ^{13}C NMR (D_2O) 146.1, 131.6, 131.4, 128.9, 77.0 (t, $^{1}J_{CP}$ = 134.2 Hz), 38.9, 33.0 (t, $^{2}J_{CP}$ = 6.0 Hz) ^{31}P NMR (D_2O): δ 18.17 (s). IR (KBr) 3426, 3027, 2924, 2855, 1497, 1454, 1175, 1063, 928, 755, 700 cm^{-1}. Anal. Calcd. for $C_9H_{12}Na_2O_7P_2$: C, 31.78; H, 3.56; P, 18.2. Found: C, 31.66; H, 3.63; P, 18.2.

(1-Hydroxy-5-phenylpentane-1,1-diyl)bisphosphonic acid **2b**: Prepared as **1a** from 5-phenylvaleric acid (2.00 g, 11.22 mmol) to give 1.57 g (39%) of **2b**. ^{1}H NMR (D_2O): δ 7.39-7.22 (5H, m), 2.70-2.63 (2H, m), 2.04-1.92 (2H, m), 1.69-1.59 (4H, m); ^{31}P NMR (D_2O): δ 18.60 (s). ^{13}C CPMAS NMR: 140.2 , 127.9, 74.6, 35.7, 24.9; ^{31}P CPMAS NMR: 25.22, 22.35, 18.72. IR (KBr) 3426, 3026, 2927, 2856, 1496, 1454, 1175, 1060, 920, 746, 699 cm^{-1}. Anal. Calcd. for $C_{11}H_{16.5}Na_{1.5}O_7P_2$: C, 36.99; H, 4.66; P, 17.3. Found: C, 36.85; H, 4.45; P, 17.5.

(1-Hydroxy-8-phenyloctane-1,1-diyl)bisphosphonic acid **2c**: Prepared as **1a** from 8-phenyloctanoic acid (0.80 g, 3.63 mmol) to give 0.47 g (36%) of **2c** as tetraacid. ^{1}H NMR (D_2O + 1 drop of 6M NaOD): δ 7.42-7.22 (5H, m), 2.68-2.59 (2H, m), 1.93-1.79 (2H, m), 1.68-1.48 (4H, m), 1.40-1.21 (6H, m); ^{31}P NMR (D_2O + 1 drop of 6M NaOD): δ 19.38 (s). ^{13}C CPMAS NMR: 142.2, 128.2, 74.0 (t, $^{1}J_{CP}$ = 143.8 Hz), 35.9, 30.5, 25.0; ^{31}P CPMAS NMR: 25.23, 21.62. IR (KBr) 3423, 3026, 2927, 2854, 1496, 1453, 1178, 1007, 942, 746, 697 cm^{-1}.

(1-Aminononane-1,1-diyl)bisphosphonic acid **4a**: A mixture of octyl cyanide (2.00 g, 14.36 mmol), phosphorus acid (2.36 g, 28.73 mmol) and benzenesulfonic acid (14.00 g) was heated to 65 °C with stirring followed by adding PCl_3 (1.3 ml, 14.36 mmol) dropwise. The mixture was maintained at 90 °C for 22 h, water (50 ml) added to the cooled mixture and stirring continued at room temperature for 2 h. The product was filtered and stirred in 2 M HCl (30 ml) overnight. After filtration, the solids were washed with EtOH and dried under vacuum to give 0.82 g (19%) of **4a** as a white solid. ^{1}H NMR (D_2O): δ 2.11-2.00 (2H, m), 1.61-1.52 (2H, m), 1.38-1.23 (10H, m), 0.90-0.82 (3H, m); ^{31}P NMR (D_2O): δ 12.71 (s). ^{13}C CPMAS NMR: 57.31, 33.6, 31.9, 29.5, 28.3, 23.8, 21.9, 14.1, 13.1; ^{31}P CPMAS NMR: 16.26, 13.01, 5.28, 1.31. IR (KBr) 2929, 2858, 1627, 1551, 1467, 1176, 1058, 923 cm^{-1}. Anal. Calcd. for $C_9H_{23}NO_6P_2$: C, 35.65; H, 7.64; N, 4.62; P, 20.4. Found: C, 36.39; H, 7.91; N, 4.56; P, 19.7.

(1-Aminodecane-1,1-diyl)bisphosphonic acid **4b**: Prepared as **4a** from decanonitrile (2.00 g, 13.05 mmol) to give 1.15 g (28%) of **4b**. ^{1}H NMR (D_2O): δ 2.06-1.96 (2H, m), 1.58-1.48 (2H, m), 1.33-1.18 (12H, m), 0.85-0.78 (3H, m); ^{31}P NMR (D_2O): δ 12.57 (s). ^{13}C CPMAS NMR: 57.4 (t, $^{1}J_{CP}$ = 134.8 Hz), 32.1, 28.7, 24.4, 21.9, 14.5, 13.9, 13.3; ^{31}P CPMAS NMR: 16.86, 15.18, 5.46, 0.84. IR (KBr) 2925, 2856, 1616, 1537, 1467, 1208, 1172, 1016 cm^{-1}. Anal. Calcd. for $C_{10}H_{25}NO_6P_2$: C, 37.86; H, 7.94; N, 4.42; P, 19.5. Found: C, 38.17; H, 8.16; N, 4.32; P, 19.6.

Heptadecane-1,1-diylbisphosphonic acid **5d**: A mixture of tetraisopropylbisphosphonate (12.10 g, 35.14 mmol) and dry THF (10 ml) was added dropwise to a solution of NaH (1.69 g, 42.17 mmol, 60% in oil) in dry THF (50 ml) followed by stirring under an argon atmosphere at room temperature for 1.5 h. 1-Bromohexadecane (10.73 g, 35.14 mmol) in THF (10 ml) was added gradually and the mixture maintained at 85 °C for 24 h. Water (150 ml) was added to the cooled mixture, the product extracted with DCM (3 × 150 ml), dried over $MgSO_4$, and the solvent removed under reduced pressure. The residue was purified by column chromatography (acetone/ethylacetate 2:1). In the last step, the isopropyl protecting groups were removed by refluxing in 4 M HCl overnight yielding **5d** (6.87 g, 49%) as a white solid. ^{1}H NMR (CD_3OD): δ 2.15 (1H, tt, $^{2}J_{HP}$ = 23.5 Hz, $^{3}J_{HH}$ = 6.0 Hz), 1.98-1.85 (2H, m), 1.66-1.56 (2H, m), 1.37-1.23 (26H, m), 0.93-0.86 (3H, m); ^{13}C NMR (CD_3OD): δ 39.3 (t, $^{1}J_{CP}$ = 126.5 Hz), 33.1, 30.8 (7C), 30.7, 30.7, 30.5 (t, $^{3}J_{CP}$ = 6.7 Hz), 30.5, 30.5, 26.8 (t, $^{2}J_{CP}$ = 4.7 Hz), 23.7, 14.4; ^{31}P NMR (CD_3OD): δ 21.80 (s). IR (KBr) 2916, 2851, 1473, 1163, 1022, 930 cm^{-1}. Anal. Calcd. for $C_{17}H_{38}O_6P_2$: C, 50.99; H, 9.56; P, 15.5. Found: C, 50.48; H, 9.78; P, 15.2.

Octane-1,1-diylbisphosphonic acid **5a**: Prepared as **5d** from 1-bromoheptane (4.12 g, 23.00 mmol) to give 2.54 g (40%) of **5a**. ^{1}H NMR (D_2O): δ 2.23 (1H, tt, $^{2}J_{HP}$ = 23.2 Hz, $^{3}J_{HH}$ = 6.0 Hz), 1.93-1.79 (2H, m), 1.59-1.50 (2H, m), 1.36-1.22 (8H, m), 0.89-0.81 (3H, m); ^{13}C NMR (D_2O): δ 40.3 (t, $^{1}J_{CP}$ = 126.3 Hz), 34.0, 31.7 (t, $^{3}J_{CP}$ = 6.8 Hz), 31.5, 31.1, 27.9 (t, $^{2}J_{CP}$ = 4.6 Hz), 24.9, 16.3; ^{31}P NMR (D_2O): δ 22.73 (s). IR (KBr) 2928, 2858, 1467, 1126, 1028, 928 cm^{-1}. Anal. Calcd. for $C_8H_{20}O_6P_2$: C, 35.04; H, 7.35; P, 22.6. Found: C, 35.07; H, 7.65; P, 22.9.

Undecane-1,1-diylbisphosphonic acid **5b**: Prepared as **5d** from 1-bromodecane (3.21 g, 14.51 mmol) to give 1.86 g (41%) of **5b**. ^{1}H NMR (CD_3OD): δ 2.16 (1H, tt, $^{2}J_{HP}$ = 23.5 Hz, $^{3}J_{HH}$ = 6.0 Hz), 1.99-1.84 (2H, m), 1.66-1.55 (2H, m), 1.39-1.22 (14H, m), 0.94-0.85 (3H, m); ^{13}C NMR (CD_3OD): δ 39.3 (t, $^{1}J_{CP}$ = 127.2 Hz), 33.1, 30.8, 30.7 (2C), 30.6 (t, $^{3}J_{CP}$ = 6.9 Hz), 30.5, 30.5, 26.8 (t, $^{2}J_{CP}$ = 4.4 Hz), 23.7, 14.5; ^{31}P NMR (CD_3OD): δ 21.90 (s). IR (KBr)

2923, 2852, 1462, 1124, 1016, 922 cm^{-1}.

Tridecane-1,1-diylbisphosphonic acid **5c**: Prepared as **5d** from 1-bromododecane (3.61 g, 14.48 mmol) to give 1.40 g (28%) of **5c**. ^{1}H NMR (CD_3OD): δ 2.14 (1H, tt, $^{2}J_{HP}$ = 23.3 Hz, $^{3}J_{HH}$ = 6.2 Hz), 1.98-1.84 (2H, m), 1.65-1.56 (2H, m), 1.37-1.22 (18H, m), 0.92-0.87 (3H, m); ^{13}C NMR (CD_3OD): δ 39.3 (t, $^{1}J_{CP}$ = 126.4 Hz), 33.0, 30.8, 30.7, 30.7, 30.7, 30.6, 30.5 (t, $^{3}J_{CP}$ = 6.9 Hz), 30.5, 30.4, 26.7 (t, $^{2}J_{CP}$ = 4.8 Hz), 23.7, 14.4; ^{31}P NMR (CD_3OD): δ 21.71 (s). IR (KBr) 2916, 2852, 1474, 1159, 1018, 929 cm^{-1}. Anal. Calcd. for $C_{13}H_{30}O_6P_2 \times 0.5\ H_2O$: C, 44.19; H, 8.84; P, 17.5. Found: C, 44.53; H, 9.00; P, 17.2.

Solubility experiments

The estimated solubility of synthesized compounds in aqueous solution was determined at constant room temperature (21.0 °C) by preparing a saturated solution in Milli-Q water without buffering. The mixture containing an excess of the compound was first agitated for 30 min with a magnetic stirrer and before taking the sample, the mixture was allowed to stand for 24 h without stirring. The sample (approx. 5 ml) was taken from the liquid above the solids, pH was measured and the sample was filtered through 0.2 μm membrane filter to remove any possible insoluble particles. Three replicates (n = 3) from these filtered sample solutions were taken for the determination of the phosphorus concentration which was measured in a spectrophotometer using the modified molybdenum blue method.[1] The measured phosphorus concentration was used for calculating the solubility of the compound.

The solubilities of compounds **3b** and **5d** were also determined as a function of pH. Either HNO_3 or NaOH solution of appropriate concentration was used for adjusting the pH of the solution and the solubility was otherwise determined as described above.

Recovery experiments

The recoveries of metal ions (Cr^{3+}, Fe^{3+}, Ni^{2+}, Cu^{2+}) were determined in a single metal solution ($C(M^{n+})$ = 1.00 mg/l, V= 0.100 l) at pH = 3.0 (adjusted with HCl or NaOH solutions) by the batch method in an excess of complexing agent (0.500 g). After 24 h of agitation with a magnetic stirrer, the mixture was filtered and the final metal ion concentration was measured by AAS. Recovery per cent of metal ion was calculated from the initial and final metal ion concentrations. Additional activated carbon (AC) supplement was used with the more water soluble compounds (**1a-d** and **2a-b**) to enhance filtration and to bind any possible soluble metal complexes. AC addition was conducted 15 min after the addition of the complexing agent. The possible collection of unbound Cr(III), Fe(III), Ni(II) and Cu(II) ions

by AC was studied separately and taken into account when calculating the recoveries.

pH experiments

The recovery of Cr(III) ions was determined as function of pH by the batch method with an excess of **3b, 5d** or Diphonix® resin in sodium form. The sample pH was adjusted with HCl or NaOH solutions and the initial metal ion concentration was measured by AAS. **3b, 5d** or Diphonix® resin (0.100 mg) was added to the sample (V = 100 ml, n = 3) and the mixture was agitated for 24 h with a magnetic stirrer. After filtration, the final metal ion concentration was determined. Recovery per cent of metal ion was calculated from the initial and final metal ion concentrations measured by AAS.

Capacity experiments

The metal complexing capacities for **3b** or **5d** and Diphonix® resin were determined separately by the batch method in the excess of metal ion ($C(M^{n+})$ = 100 mg/l) at pH 4.0 and otherwise as described above. The uptake of metal ions was calculated from the initial and final metal ion concentrations measured by AAS and mass of **3b**, **5d** or Diphonix®.

Regeneration experiments

Regeneration and re-adsorption experiments were accomplished by sucking in turns 25 ml Cr(III) solution (100 mg/l) and 25 ml 2.0 M HCl solutions through **3b** or **5d** (0.500 g) in glass filter crucibles (G4). The chromium concentration in the filtrate and permeated HCl solution were measured by AAS.

Tannery effluent experiments

The pH of waste water samples was measured and initial metal concentrations were measured by ICP-OES. Complexing agents **3b**, **5d** or Diphonix® (m = 1.000 g) were added to the subsample (V = 0.050 l). After 24 h agitation with a magnetic stirrer, the mixture was filtered and final metal ion concentration was measured by ICP-OES. The removal per cent of metal ion was calculated from the initial and final metal ion concentrations.

Interaction experiments

To the synthetic unary, binary and ternary solutions (V = 0.100 l) of Cr(III) (2 mg/l), Mg(II) and Ca(II) of equal molarities ($C(M^{n+})$ = 38.5 μM, V = 100 ml) complexing agent **5d** (m = 0.100 g) was added. Otherwise samples were treated and results calculated similar way as in the case of tannery effluents, except that metal concentrations were measured by AAS. Also, ternary solution where Cr:Mg:Ca molar ratio was 1:10:10 was made and tested.

Agitation time experiments

The removal per cent of Cr(III) ions with **3b, 5d** and Diphonix® was determined as a function of time by agitating the Sample 2 solutions for 5, 10, 30, 60, 150 and 1440 min and taking a sample in every time point. Other conditions were the same as **i**n Tannery effluent experiments. Chromium concentrations were measured by AAS. Similar experiments were made also with pure Cr solution (2.8 mg/l).

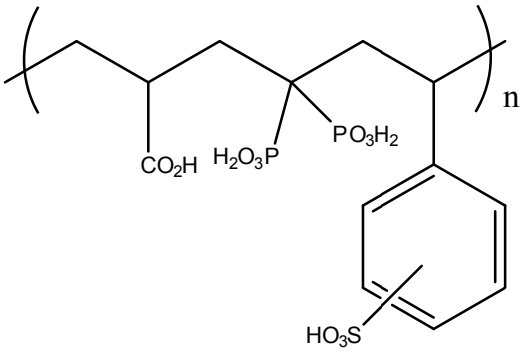

Fig. S1 Structure of Diphonix® resin.[11]

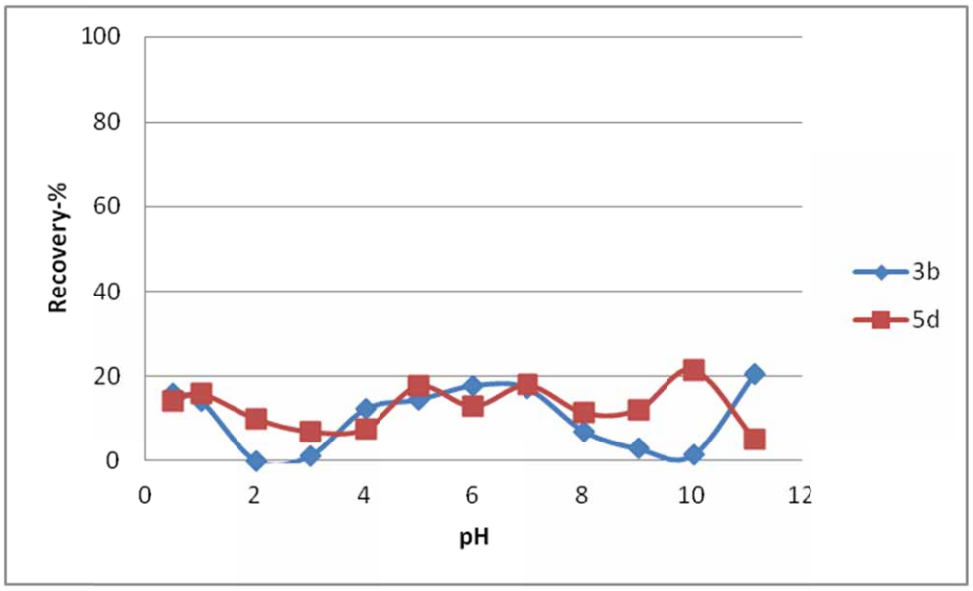

Fig. S2 The effect of pH on collection of Cr(VI).

Table S1 The effect of Cr, Mg and Ca on their removal by **5d** ($C(M^{n+})$ = 38.5 μM).

	Removal (%)		
Matrix	Cr	Mg	Ca
Cr	98.7	98.5	77.2
Mg	98.2	96.9	76.9
Ca	97.9	97.1	80.2
Cr+Mg+Ca	96.6	98.0	79.1

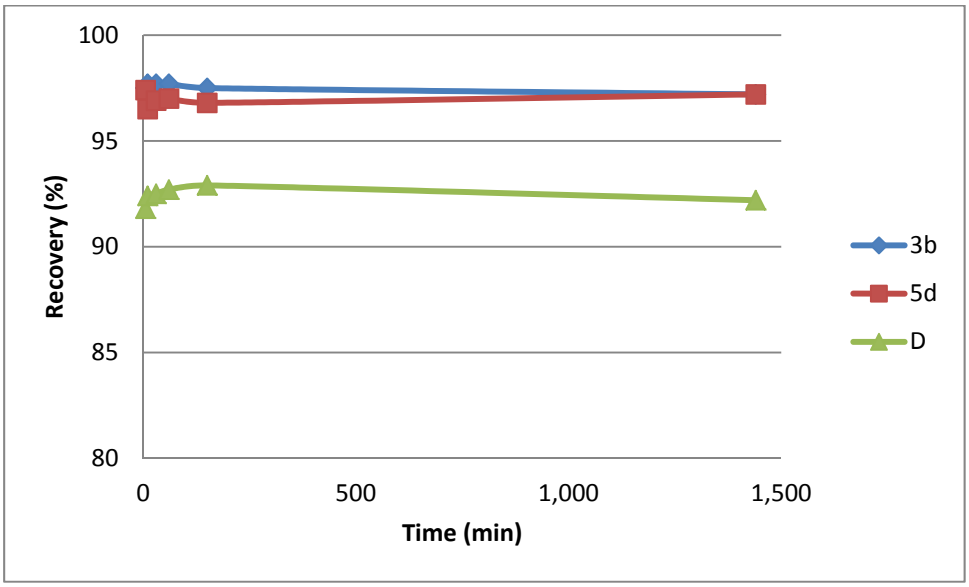

Fig. S3 The effect of agitation time on the binding of Cr(III) from synthetic Cr solution.

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