



# Synthesis, characterization and physicochemical studies of new chelating resin 1, 8-(3, 6-dithiaoctyl)-4-polyvinylbenzenesulphonate (dpvbs) and its metallopolymer Cu(II), Ni(II), Co(II) and Fe(III) complexes

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## ABSTRACT

A new chelating resin, 1,8-(3,6-dithiaoctyl)-4-polyvinylbenzenesulphonate (dpvbs) has been synthesized by coupling Amberlite XAD-16 with (2,2'-ethylenedithio) diethanol using pyridine/CH<sub>2</sub>Cl<sub>2</sub> mixture as a solvent. The chelating resin and its metallopolymer Cu(II), Ni(II), Co(II) and Fe(III) complexes have been synthesized and characterized by EDS, SEM, XPS, elemental analysis, spectral (IR, UV/Vis, EPR). The thermal analysis of the resin and its metallopolymer complexes indicated an endothermic spontaneous sorption mechanism with the liberation of water of hydration of the metal ions and that adsorbed by the free resin. At the solid liquid interface, the degrees of freedom increased during the sorption of the metal ions onto the resin. The surface area of polymer support and its metallopolymer complexes are estimated by (BJH) method. The batch equilibrium method was used for studying the metal sorption and selectivity at different pH values and different contact times at room temperature. ICP-AES was used to estimate the metal capacity of the resin for sorption of Cu(II), Ni(II), Co(II) and Fe(III) from aqueous solutions utilizing the batch equilibrium method. The sorption tendency of the metal ions by the resin was found to be: Cu(II) > Fe(III) > Co(II) > Ni(II). Adsorption kinetics was found to be fit the pseudo-second order model.

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## 1. Introduction

It was reported that the solid phase extraction (SPE) has several advantages over the usual liquid extraction techniques. This is due to: (i) its direct and ease application for very small size (micro liter volume) without any sample loss, beside it is simple, fast and waste-less generation (ii) saving time and cost. However, SPE is usually interfaced with major chromatographic techniques either in the form of on-line or off-line mode [1–3]. Chelating polymeric matrices, termed as polychelators (PC) has been used in SPE technique [2]. These chelating polymeric matrices have several highlighting Characteristics such as versatility, durability, a high degree of selectivity, enhanced hydrophilicity and good metal loading capacity [3,4]. The donor atoms; oxygen, nitrogen, phosphorous and sulphur that can form complexes with different metal ions are present in functional groups of different organic

compounds [2]. The activity of the loaded group [5], the size of the modifier [1] and the characteristics of hard-soft acid-base [5,6] are the main factors that determine the selectivity of the surface of the chelating resin. Several chelating supports using polystyrene-divinylbenzene (PS-DVB) resins were found to be fruitful [7–24] as they can be easily loaded with different function groups-containing ligands [3,14–24]. These resins beads are commercially available as Amberlite XAD series, with different degree of cross-linkage, bead size and pore diameters that are strongly affecting the rate and the extent of adsorption capacity. Several chelating matrices were developed using modified Amberlite XAD series because of their advantages over other supports. These advantages are; (i) high surface area as chemical homogeneous non-ionic structure, (ii) porosity and uniform pore size distribution, (iii) good sorption properties for great amounts of neutral compounds [25]. The most widely support materials for the synthesis of chelating resins are XAD-2, XAD-4 and XAD-16 [14,26–28]. The large surface area also makes it possible to increase the number of donor sites making them more accessible towards metal sorption. Amberlite XAD-16 upon ligand immobilization affords chelating

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resins of better sorption capacities over the others because of its higher surface area. The type of interaction between the modified resin and metal ions can be chemical or physical interaction, this is usually predicted by spectroscopic techniques as well as the adsorption isotherm studies [10,14,20,25,26]. In order to design new chelating resins with high metal capacities and selectivity towards different metal ions, greening the extraction process by replacing the use of large quantities carcinogenic solvents which are used in a liquid-liquid extraction, with an added reusability of the modified resin, and in continuation of our research in this area, we aim to: (i) synthesize the newly chelating resin 1,8-(3,6-dithiaoctyl)-4-polyvinylbenzenesulphonate (dpvbs), (ii) study its ligating behavior towards Cu(II), Ni(II), Co(II) and Fe(III) (iii) characterize the synthesized chelating resin and its metallopolymer complexes and (iv) study their metal capacities by batch methods utilizing ICP-AES for metal ion concentration determination.

## 2. Materials and methods

### 2.1. Materials

All the chemicals used in this work were of analytical grade of Merck (Germany). Commercially, available Amberlite XAD-16 (specific area  $800 \text{ m}^2\text{g}^{-1}$  and bead size 20–60 mesh) was obtained from Aldrich and it was thoroughly washed by  $4.0 \text{ mol L}^{-1}$   $\text{HNO}_3$ ,  $1.0 \text{ mol L}^{-1}$   $\text{NaOH}$  and double distilled water successively and well dried before use. Chlorosulphonic acid, thionyl chloride and 2,2'-(Ethylenedithio)diethanol were purchased from Aldrich and used as received.  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$  were purchased from Aldrich and used without further purification. Working metal ion solutions ( $0.1 \text{ mol L}^{-1}$ ) of Cu(II), Ni(II), Co(II), and Fe(III) were prepared by dissolving the accurate weight of the corresponding metal(II) nitrate in acidified double distilled water. The glassware used were soaked in 10%  $\text{HNO}_3$  overnight before use and cleaned repeatedly with double distilled water.

### 2.2. Synthesis of chelating resin, 1,8-(3,6-dithiaoctyl)-4-polyvinylbenzenesulphonate

In a closed system, a solution of 2,2'-(ethylenedithio)diethanol, EDTDE, (3.83 g; 20 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 mL) mixed with pyridine (10 mL) was added slowly with stirring to  $\text{Ps-SO}_2\text{Cl}$  (10.7 g; 45 mmol) which was synthesized according to the previously reported method [17,29]. The reaction mixture is cooled to  $-5 \pm 1 \text{ }^\circ\text{C}$  with maintaining the temperature at  $-5 \pm 1 \text{ }^\circ\text{C}$  during the addition. The mixture was kept close at this temperature for 6 h and then stand without reflux or stirring for 48 h at room temperature. The resin was filtered off, washed with  $\text{CH}_2\text{Cl}_2$  ( $5 \times 20 \text{ mL}$ ) followed by  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  ( $5 \times 20 \text{ mL}$ ) and dried under vacuum at  $60 \text{ }^\circ\text{C}$  for 48 h.

**Elemental analysis:** % Calculated (% Found): C: 46.48 (46.85), H: 5.63 (4.62), S: 22.54 (22.40) confirming the repeating unit formula  $[\text{dpvbs} \cdot 3\text{H}_2\text{O}]_n$  or  $(\text{C}_{22}\text{H}_{26}\text{S}_4\text{O}_6 \cdot 3\text{H}_2\text{O})_n$ .

### 2.3. Synthesis of the metal complexes

The metal complexes were synthesized according to the following general method. To an aqueous solution (100 mL containing 200 mg, (0.68–0.86) mmol) of  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Fe}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$  adjusted at pH 5.5, 6.0, 6.0 and 4.8, respectively, the chelating resin (300 mg, 0.51 mmol) was added. The reaction mixture was stirred at room temperature for 8–12 h and kept overnight at the same temperature. The mixture was filtered off, washed several times with water (150 mL;  $5 \times 30 \text{ mL}$ ), followed by diethyl ether (150 mL,

$10 \times 15 \text{ mL}$ ), dried under vacuum at  $60 \text{ }^\circ\text{C}$  for 24 h and kept in a vacuum desiccator over  $\text{P}_2\text{O}_5$

### 2.4. End group tests

The existence of OH as an end group in the synthesized **1,8**-(3,6-dithiaoctyl)-4-polyvinylbenzenesulphonate (dpvbs) was tested by the following reactions:

- (1) A 0.5 g resin was mixed with 15 mL glacial acetic acid in presence of 1 mL concentrated  $\text{H}_2\text{SO}_4$  in a round bottled flask and refluxed for 6 h on a hot plate. After cooling to room temperature, the solid was filtered off and washed several times with water until acid-free, followed by diethyl ether and dried under vacuum at  $60 \text{ }^\circ\text{C}$  for 24 h. The IR spectrum was recorded to detect the possibility of formation of ester end group.
- (2) A mixture of 0.5 g resin and 15 mL of 2 M ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) solution in presence of 1 mL concentrated  $\text{H}_2\text{SO}_4$  in a round bottled flask was refluxed for 3 h on a hot plate and cooled to room temperature. The solid was filtered off, washed several times with water until acid-free, followed by diethyl ether and dried under vacuum at  $60 \text{ }^\circ\text{C}$  for 24 h. The IR spectrum was recorded to detect the possibility of formation of aldehydic end group.

### 2.5. Physical and spectroscopic measurements

CHNS analysis was performed on LECO CHNS-932 elemental analyzer. The concentration of the metal ions was determined by ICP-AES. A digital Orion pH/ISE meter-model 710 A, was used for the pH measurements. The pH ranges of 2.5–4 and 4–7 of the solutions were adjusted utilizing monochloroacetic acid/acetate and acetate buffers, respectively. HCl was used to adjust the pH below 2.5 while NaOH was used for adjusting the pH above 7.0. The FT-IR spectra of the chelating resins and their metal complexes as KBr pellets were recorded with a Shimadzu 2000 FT-IR spectrophotometer. Electronic spectra of the complexes recorded as nujol mulls were accomplished by Varian Cary-5 double beam spectrophotometer. The EPR spectrum for the copper complex was recorded on a Radiopan Varian spectrometer T 100.0000 kHz and at different G modulation amplitude with a rectangular TE 102 cavity and 100 kHz modulation field. Resonance conditions were found at ca. 9.7 GHz (X-band) at room temperature. The field was calibrated with a powder of diphenylpicrylhydrazyl free radical (DPPH;  $g = 2.0037$ ). Thermal analyses were carried out on a Shimadzu thermal system 50 consisting of TGA-50 and DTA-50 in the temperature range of room temperature up to  $1000 \text{ }^\circ\text{C}$  under dinitrogen atmosphere and heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$ . The surface area of polymer support and its metallopolymer complexes were characterized using the automatic physico sorption analyzer Micromeritics ASAP 2010, by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods through  $\text{N}_2$  adsorption-desorption. The metal ion dispersion and morphology of the chelating polymer and its complexes were recorded by scanning electron microscopy (SEM) by JSM – 6300, JEOL Co., Tokyo, Japan, electron microscope, operating at 20 kV with an energy dispersive spectroscopy (EDS) X-ray spectrometer BRUKER AXS – Microanalysis GMBH- Berlin, Germany. X-ray photoelectron spectrometry, (XPS) measurements were conducted on a VG ESCALAB 200 (UK) spectrometer using  $\text{MgK}\alpha$  radiation 1253.6 eV operating at 300 W (15 kV, 20 mA). All binding energy values were determined with respect to C1s line (284.6 eV) obtained from adventitious carbon. Depth profiling was done with an Ar ion gun with 5 kV energy and

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