



Biogenic glutamic acid-based resin: Its synthesis and application in the removal of cobalt(II)



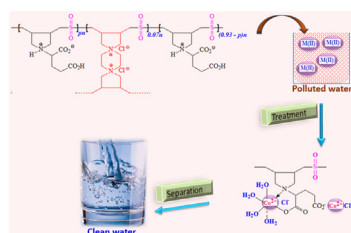
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HIGHLIGHTS

- A novel resin embedded with metal chelating glutamic acid was synthesized.
- The biogenic amino acid residues imparted remarkable efficacy to remove Co(II).
- The resin showed excellent ability to remove various metals from wastewater.

GRAPHICAL ABSTRACT



A novel resin embedded with biogenic glutamic acid residues to chelate toxic metal ions

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ABSTRACT

Inexpensive biogenic glutamic acid has been utilized to synthesize a cross-linked dianionic polyelectrolyte (CDAP) containing metal chelating ligands. Cyclooligomerization, using azoisisobutyronitrile as an initiator, of *N,N*-diallylglutamic acid hydrochloride, sulfur dioxide and a cross-linker afforded a pH-responsive cross-linked polyzwitterionic acid (CPZA) which upon basification with NaOH was converted into CDAP. The new resin, characterized by a multitude of spectroscopic techniques as well as Scanning Electron Microscopy (SEM) and Brunauer–Emmett–Teller (BET) analyses, was evaluated for the removal of Co(II) as a model case under different conditions. The adsorption capacity of 137 mg g^{-1} does indeed make the resin as one of the most effective sorbents in recent times. The resin leverages its cheap natural source and ease of regeneration in combination with its high and fast uptake capacities to offer a great promise for wastewater treatment. The resin has demonstrated remarkable efficiency in removing toxic metal ions including arsenic from a wastewater sample.

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1. Introduction

Water pollution is gaining increasing international awareness since industries are on the upward growth and oftentimes wastes are discharged to the environment without sufficient precautions. Sources such as mining, metal plating, battery, and paper industries are responsible for introducing these discharges into the environ-

ment [1]. Several ions of the heavy metals are not only toxic to living organisms in water but also, cause harmful effects to terrestrial animals. Cobalt is among the common toxic metals that are used extensively in various human endeavors [2]. Excessive levels of cobalt in the body lead to cobalt poisoning; however, in minute amounts, it is an essential component of Vitamin B₁₂ which is needed for the smooth functioning of many important body processes and it is depleted only during pernicious anemia [3]. Chronic exposure to cobalt has numerous deleterious effects on human health [4,5]. Low levels of cobalt exposure have been reported to impact lung function, induce occupational asthma [6,7], vision and hearing problems, especially in patients with hip implants con-

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taining cobalt [8,9]. Very recently, the US department of health and human services in its 14th report on carcinogens has classified cobalt and cobalt compounds that release cobalt ions in Vivo as reasonably anticipated to be a human carcinogen [10].

Although different treatment techniques such as precipitation, membrane technology, ion-exchange, electrocoagulation have been reported [11,12] to remove effluents in aqueous media, adsorption [13,14] seems to have a greater potential for such application. Since the adsorption performance is limited by material design and properties, strong efforts have been made in exploring the structural properties of various materials. The use of inorganic materials in combination with polymer hybrid materials for adsorption has been considered as promising, as it is effective, economical as well as environmentally friendly in removing pollutants from the water [15,16].

A recent review described polyglutamic acid (PGA) as an emerging biopolymer of commercial interest because of its prospective wide applications in healthcare, foods and pharmaceuticals [17]. In wastewater treatments, PGA and other poly-amino acids have demonstrated incredible potentials in removing toxic metal ions [18–21]. Poly amino acids remove toxic metal ions through chelation and electrostatic binding [22]. The electrostatic binding of heavy metals by PGA has also been explored for possible treatment of metal intoxication in humans [23,24]. Other researchers have also shown the capability of PGA as a sorbent for removing cationic dyes from waste water [25] thus demonstrating its versatility in removing both inorganic and organic pollutants, especially from aqueous media.

In PGA, two of the three functionalities of the amino acid are involved in the formation of peptide (i.e. amide) bonds thereby keeping only the side chain carboxylate for the purpose of metal exchange. It is our objective to exploit the cheap natural source of the biogenic amino acid and its three metal chelating functional motifs to design and synthesize a polymeric material keeping intact the integrity of all three original chelating functionalities of glutamic acid. This work thus reports the synthesis of such a new glutamic acid-based resin as a sorbent for sequestering Co(II) as a model case from aqueous solution using sorption kinetics and several isotherm models.

2. Experimental

2.1. Chemicals and materials

L-Glutamic acid, piperazine, allyl chloride, obtained from Fluka Chemie AG, were used as received. Azobisisobutyronitrile (AIBN, Fluka AG) was crystallized from chloroform–ethanol. Dimethylsulfoxide (DMSO) was dried using calcium hydride and then distilled under reduced pressure (64–65 °C, 4 mm Hg). Cobalt(II) chloride hexahydrate (CoCl₂·6H₂O, Fluka AG) was used to prepare the standard which was subsequently diluted to the required concentrations. Sodium hydroxide and nitric acid were purchased from Sigma–Aldrich. Millipore water (18.2 MΩ cm) was used for the adsorption study. For the real wastewater study, the industrial wastewater was collected from an industrial area in Dammam KSA, then, it was filtered to remove the large particles and soils. The pH of the industrial wastewater was determined to be 6.3. The industrial wastewater was spiked with 20 mg/L Co(II) in order to test the performance and efficiency of the analytical method in the real wastewater matrix.

2.2. Physical methods

A Perkin–Elmer 16F PC FTIR spectrometer was utilized to record IR spectra. The proton and carbon-13 spectra were recorded on

a JEOL LA 500 MHz spectrometer using HOD signal at δ4.65 ppm and dioxane signal at 67.4 ppm as internal and external standards, respectively. The resin surface morphology before and after the cobalt(II) adsorption was examined by Field emission scanning electron microscope (FESEM) and their elemental analyses were determined using Energy-dispersive X-ray spectroscopy (EDX) fitted with a detector model X-Max. A Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer was used to carry out the elemental analysis. The concentration of Co(II) was monitored using a flames atomic absorption spectrometer (FAAS) (Thermo scientific iCE 3000). Thermogravimetric analysis (TGA) was conducted in a thermal analyzer (SDT Q600 from TA instruments, USA). The temperature was raised at a rate of 10 °C/min with air flowing at a rate of 100 mL/min. The methods of Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) were adopted to determine the resin surface area and its pore size distribution, respectively.

2.3. Synthesis of the starting materials

Glutamic acid-derived monomer **1** was prepared as described [26]. The preparation of cross-linker **2** is described elsewhere [27].

2.3.1. Polymerization process

Sulfur dioxide (2.12 g, 34.5 mmol) was absorbed onto a solution of cross-linker **2** (0.721 g, 2.26 mmol) and monomer **1** (7.91 g, 30 mmol) in DMSO (11.3 g) in a RB flask (50 mL). After adding the initiator AIBN (160 mg), the reaction mixture under N₂ was stirred at 60 °C for 48 h. The resultant cross-linked polyzwitterionic acid (CPZA) **3** was soaked in excess water for 24 h, filtered and dried under vacuum at 60 °C to a constant weight (8.94 g, 83%). (Found: C, 44.8; H, 6.1; N, 4.8; S, 10.9%). A terpolymer from monomer **1** (- HCl) (93 mol%), cross-linker **2** (7 mol%) and SO₂ (107 mol%; each cross-linker is expected to react with 2 equivalents of SO₂) requires C, 45.18; H, 5.91; N, 4.91; S, 11.24.

2.3.2. Conversion of CPZA **3** to cross-linked dianionic polyelectrolyte (CDAP) **4**

CPZA **3** (8.46 g, 28.2 mmol) in water (150 cm³) was treated with NaOH (1.7 g, 42.5 mmol) at 20 °C for 1 h. A second portion of NaOH (1.7 g, 42.5 mmol) was added, and the mixture was stirred for an additional hour. The resultant resin **4** was filtered and washed with water and acetone and dried at 60 °C under vacuum (9.2 g, 96%). (Found: C, 39.5; H, 4.9; N, 4.2; S, 9.6%). The resin containing the units derived from monomer **1** (93 mol%) and monomer **2** (7 mol%) and SO₂ (107 mol%) requires C, 39.93; H, 4.71; N, 4.36; S, 9.98.

2.4. Co(II) adsorption on CDAP resin

Adsorbent CDAP **4** (30 mg) was added into an aqueous Co(II) solution (20 mL) of specific concentration of 20 or 30 or 50 or 100 mg L⁻¹ and then stirred for a period of 10, 20, 30, 60, 90 and 120 min at 298 K. The filtrate after each time interval was analyzed by AAS to determine the Co(II) uptake. Using an initial Co(II) concentration of 50 mg L⁻¹, the pH dependency of the adsorption process was evaluated at 298 K, while the experiments at 298, 318 and 338 K were performed to determine the kinetic and thermodynamic parameters. The percentage removal of Co(II) is computed using Eqs. (1) and (2):

$$q_t = \frac{(C_i - C_t)V}{W} \quad (1)$$

$$\%Co^{2+} \text{ uptake} = \left(\frac{C_i - C_t}{C_i} \right) \times 100 \quad (2)$$

where, C_i and C_t represent the initial and final Co(II) concentrations (mg L⁻¹), respectively; V and W denote the solution volume (L) and

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