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Synthesis of hydrophobic cross-linked polyzwitterionic acid for simultaneous sorption of Eriochrome black T and chromium ions from binary hazardous waters

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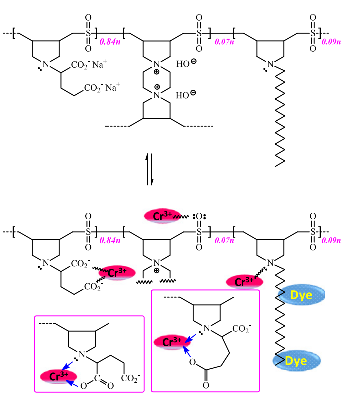
GRAPHICAL ABSTRACT



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ABSTRACT

Hydrophobic cross-linked polyzwitterionic acid (HCPZA) containing long chain (C_{18}) hydrophobes and residues of a glutamic acid having unquenched nitrogen valency was synthesized. Exploiting the chelating ability of the amino acid residues to scavenge toxic metals and the hydrophobic surface to scoop up the organic contaminants, the resin HCPZA was evaluated for simultaneous removal of chromium and Eriochrome black T (EBT) from wastewaters. The structure and morphology of the polymer before and after sorption were characterized by using FTIR, TGA, EDX and SEM. The effect of various parameters such as contact time, pH and initial concentrations were investigated to arrive at optimum conditions. The adsorption of Eriochrome black T and Cr (III) on HCPZA reached equilibrium in 30 min. The mechanism of adsorption was investigated using kinetic, diffusion and isotherm models. The adsorption kinetic data were described well by the pseudo-second order model and by the Freundlich isotherm model. EDX analysis confirmed the adsorption of Cr (III) and EBT on the polymer. The hydrophobic resin exhibited a remarkable simultaneous adsorption capacity for EBT and Cr (III) and thus demonstrated its potential to be a promising adsorbent for removal of dyes and heavy metal ions from wastewaters.

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1. Introduction

Apart from the agricultural sector, chemical-intensive industries are the second major contributor of environmental pollution. One such contributor is the textile industry that uses a large amount of water due to its nature of being chemical intensive for numerous processes that generate a lot of organic effluents that end up in water bodies [1]. Coloration and related activities by these industries using dyes to give fabric various colors that are appealing to human comes with a lot more just "Color the earth beautifully and kill it with a sweet poison" as mentioned by [2]. Pharmaceutical, food, Pulp Mill and tannery Industries contributed handsomely add to this form of pollution. Dyes uses by these industries are designed for a particular purpose making them synthetic in nature. Even though we encounter them in food and drugs preparation, they are a potential hazard to living organisms as most of them are very toxic, cancer causing, mutagens and teratogen [3]. The major problem encounter in the conventional treatment plants when it comes to dyes is their stability toward the light (no photolytic degradation by sunlight), resistant to microbial degradation and temperature [4]. Moreover, it is aggravated by the presence of another substance apart from the dyes like heavy metals (Cr^{6+}, Cd^{2+}, Zn^{2+}, and Fe^{3+} etc.). This makes their detection as well as removal very hard. A number of treatment methods for wastewaters polluted by organic pollutants, have been used such as photolytic degradation, precipitation, electrocoagulation, and membrane filtration and reverse osmosis to remove both classes of organic pollutants and heavy metals [5–8]. Each of the above-mentioned technology has its own limitation in terms of energy use, large chemical requirement, and efficiency. One of the technologies receiving attention today is the adsorption process. The adsorption process gives the advantages of being effective, low-cost and non-production of by-product that might be more dangerous than the parent pollutant [9–11]. Activated carbon has so far proved to the very best in the area of water treatment as a good adsorbent. Adsorption using activated carbon synthesized from rice hull waste was reported for the removal of EBT [12] with a removal of 93.4%. The use of plasma and electromagnetic radiation to enhance the removal of EBT was investigated [13]. Bedoui and his group use the combination of oxidation processes for the treatment of EBT [14]. The application of magnetic nanoparticles were reported for the removal of Acridine orange dye and EBT [3,15]. In the removal of methylene blue dye, Scolymus Hispanicus bark was utilized for EBT removal in aqueous media [16]. β-cyclodextrin/Polyurethane polymer foam was reported to remove EBT up to 93.14% at optimum conditions [17].

Zwitterionic polymers have attracted attention in recent years due to their chelating ability for pollutants. Cross-linked polymers are promising for water treatment plants worldwide with some of the few studies conducted [18]. Many studies on decontamination of water by pollutants is narrow to only the single component, however, few studies have been carried out to remove contaminants in complex systems which reflect actual environmental pollution. The use of hydrophobic ionic liquids for the separation of methyl blue and Cr^{6+} was reported [19]. A mechanistic approach was reported for using succinic-grafted chitosan for the removal of basic dye and zinc simultaneously [20]. Microbial bioaccumulation of Reactive Black-B dye and chromium (VI) was reported [21]. The use of magnetic-graphene composite for the treatment of Cd^{2+}, methylene blue, and orange G dyes was reported [22]. Simultaneous removal of Cu^{2+} and phenol on modified polymethacrylated [23].

This work aimed to use glutamic acid in a new role by incorporating it in a resin that can scavenge toxic metal ions with the assistance from its trivalent nitrogen. Glutamic acid, one of the 20–23 proteinogenic amino acids, is of immense importance in a variety of ways. Glutamate is a key compound in cellular metabolism; it is used as a food additive since it enhances flavor. The derivatives of glutamic acid have etched a place of distinction in chelation technology to detoxify toxic metal ions [23].

For this purpose, we would like to exploit Butler's cyclopolymerization protocol [24] in synthesizing and polymerizing hydrophilic monomers **1**, hydrophobic monomers **2**, and cross-linker **3**, with SO_2 as the fourth monomer. Note that the incorporation of the hydrophobic and hydrophilic monomers into cross-linked polymer serves dual purposes: simultaneous removal of toxic metals as well as organic contaminants from wastewater. In a single treatment, it would exploit the chelating ability of glutamic acid residues to remove metal ions and the hydrophobic surface of long chain (C_{18}) hydrocarbons to scoop up the organic contaminants. We anticipate an exciting outcome of this novel proposition, which envisages the use of the novel resin in the simultaneous removal of EBT and chromium.

2. Experimental

2.1. Material and methods

A standard stock solution of Chromium (III) (1000 mg/L), hydrochloric acid, nitric acid and sodium hydroxide were used from Sigma-Aldrich and are of analytical grade. Eriochrome black T dye form. The standard stock solutions were diluted to various concentrations as required for the experiment. An organic Tertiary butyl hydroperoxide (TBHP) (with 70 w/w% in water), diallylamine (⩾98% purity), piperazine (97% purity), allyl chloride (98% purity), 1,3-propanesultone (⩾98% purity) from Fluka (AG) were used without purification as received. Hydrophobic monomers **2** [24] and cross-linker **3** [25] were synthesized using literature procedures [24,25]. Monomer **1** was prepared in our laboratory using by reacting dimethyl glutamate with allyl chloride followed by hydrolysis of the ester groups. Reagents were purchased from commercial vendors and are of analytical grade. Laboratory wares used in this experiment are in-house and are of the required standard. Distilled water was utilized throughout.

2.2. Analytical methods

Physical methods like, Energy-dispersive X-ray spectroscopy (EDX) gives the elemental information about the polymer. Scanning electron microscopy (SEM) was used for surface morphology and FT-IR spectra were determined IR spectra on Perkin-Elmer spectrometer. Thermogravimetric measurements (TGA) were performed using an SDT analyzer TA, USA. BET surface area analyzer for the specific surface area measurements, pore size diameter, and pore volumes. Brunauer–Emmett–Teller (BET) in cooled N2 method by BET surface area analyzer was employed for the specific surface area measurements.

2.3. Synthesis of the resin

Tetrapolymerization of monomers 1–3 and SO_2 to hydrophobic cross-linked polyzwitterionic acid (HCPZA) 4 was performed by the following steps (see Scheme 1). Briefly, to a solution of **1** (8.45 g, 32 mmol), **2** (1.37 g, 3.56 mmol), and **3** (0.855 g, 2.68 mmol) in dimethyl sulfoxide (14.5 g) in a round bottom flask (50 cm^3) was absorbed SO_2 (2.62 g, 41 mmol). Initiator AIBN (250 mg) was added and the mixture was stirred in the closed flask at 65 °C for 48 h. A few times the flask was opened to release gaseous product N_2. The transparent gel was soaked in water and was repeatedly washed