Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

Novel hyperbranched polyurethane resins for the removal of heavy metal ions from aqueous solution

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ARTICLE INFO

Article history:
Received 19 September 2015
Received in revised form 23 July 2016
Accepted 10 August 2016
Available online 20 August 2016

Keywords:
Polyurethane (PU)
Adsorption
Isotherm
Kinetic
Thermodynamics
Heavy metal ions

ABSTRACT

Novel polyurethane (PU) resin was studied for removal of Pb(II) and Ni(II) ions from aqueous solution. The resin was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, TGA, SEM, EDAX and DLS analysis. The optimization of experimental conditions and parameters including pH, adsorbent dosage, contact time, and initial metal ion concentration for the removal of heavy metal ion was evaluated. Batch adsorption kinetic studies were mathematically described, and it has been found that the adsorption of Pb(II) and Ni(II) ions onto the PU follow the pseudo-second order kinetic model. Adsorption isotherms have also been studied, and the data fitted well in the order of the Freundlich > Temkin > Sips > Langmuir isotherm models. The maximum adsorption capacities of PU for Pb(II) and Ni(II) ions were calculated from the Langmuir isotherm, 236.5 and 217.5 mg/g respectively. Thermodynamic parameters such as, ΔH° and ΔG° suggest that the adsorption of Pb(II) and Ni(II) ions onto PU is exothermic and spontaneous in nature. The adsorption efficiency of the PU was retained even after five cycles. The PU has good adsorption efficiency for the removal of Pb(II) and Ni(II) ions compared to other adsorbents.

1. Introduction

Metals and their compounds are indispensable to the industrial, agricultural and technological development of every country. Industrial processes and used commercial metallic products produce more amounts of metallic waste products, which are discharged into the water or land-dump sites. Environmental contamination with heavy metal ions is a serious problem owing to their tendency to accumulate in living organisms and toxicities in relatively low concentration (Murugesan et al., 2014; Denizil et al., 2000; Shukla et al., 2006; Muthukrishnaraj et al., 2015). Many methods, such as reduction and precipitation, ion exchange, reverse osmosis and adsorption, have been proposed to remove heavy metal ions from waste water. Among these technologies, many researchers concentrated on metal ion recovery using chelating polymers because they are reusable, easy handling and have higher adsorption capacities, efficiencies as well as high selectivity to some metal ions (Gode, 2003; Prasun et al., 2003; Kavakl et al., 2005; Bahire and Niyazi, 2001; Kais and Suhaila, 1997; Saima et al., 2005a). Chelating resins are typically characterized by functional groups containing O, N, S and P donor atoms which coordinate to different metal ions. Chelating ion exchange resin, in general, coordinating copolymers possess covalently bonded side chains which contain one, two or more (multiple) donor atoms. Due to this fact, as a Lewis base, they are able to form coordinating bonds with Lewis acids such as the most toxic metal ions. The chelating group in the polymer chain with donor atoms act as Lewis base and the metal ions with positive charge act as Lewis acid. The coordination-type bonds between the chelating resins and the metal ions have high selectivity toward commonly encountered

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http://dx.doi.org/10.1016/j.psep.2016.08.010

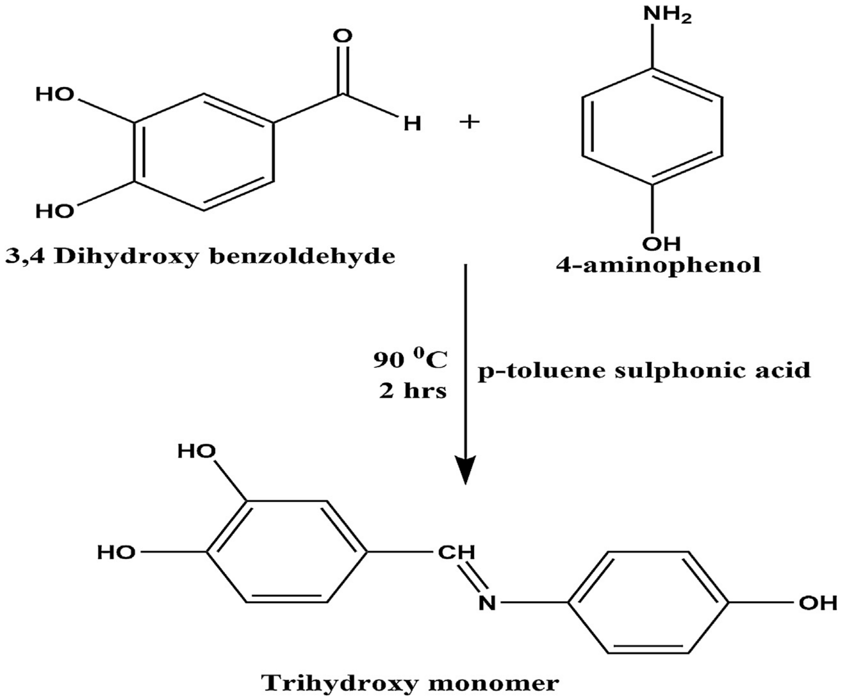

Fig. 1 – Synthesis of trihydroxy monomer.

metal ions, M(II). The sorption efficiency mainly depends on the types of resin functional groups and to a smaller extent on resin beads size and its other physicochemical properties. Hence, numerous chelating resins have been prepared through the polymerisation of conventional chelating monomers, such as acrylic acid (Li et al., 2002), allylthio urea (Kilic et al., 2005), vinyl pyrrolidone (Essawy and Ibrahim, 2004) and vinyl imidazole (Pekel et al., 2002). Chelating resins with picolylamine (Wolowicz and Hubicki, 2012), amino salicylic acids (Dissouky et al., 2011) and melamine-formaldehyde (Baraka and Heslop, 2007) functional groups have also been successfully used for the removal of heavy metal ions.

Our group is concentrating on synthesis of stable, highly efficient and higher regeneration capacity chelating polymeric resins based on polyamines, polyacrylamide (Murugesan et al., 2011; Dinesh Kirupha et al., 2013; Ravikumar et al., 2010; Kalaivani et al., 2014a) and chemically modified cellulose (Saravanan and Ravikumar, 2015). Important requirement of such polymeric resins include its resin stability in different environmental conditions, high adsorption capacity and molecular rigidity. In the recent past polyurethane composites such as multiwalled carbon nano tube-polyurethane (Khan et al., 2015), polyurethane-hydroxyapatite (Jang et al., 2008) were reportd for the removal of Pb(II) ions from aqueous solutions. Polyurethane membranes such as polyurethane-keratin (Manrique-Juárez et al., 2013; Saucedo-Rivalcoba et al., 2011) were found to be efficient one for the removal of Cr(VI) ions from water. Polymers containing azomethaine groups can also be used for rebar corrosion (Bhuvaneshwari et al., 2015). Purpose of this study is to synthesize high rigid hyperbranched polyurethane resin and to test its ability toward adsorption of heavy metal ions from aqueous solutions. The synthesized polyurethane can also be used for rebar corrosion in concrete structures.

2. Materials and methods

2.1. *Chemicals and reagents*

3,4-Dihydroxybenzaldehyde (Aldrich), *p*-hydroxyaniline (Fluka) and 4,4′-methylenediisocyanate (MDI) were used as received. Dimethylformamide (DMF) (Himedia) was stored over KOH and distilled under reduced pressure. Absolute ethanol was obtained by refluxing the commercial ethanol with quick lime for 12 h and then distilled. All other solvents and reagents used were either of analytical grades or purified according to the standard procedure. $Pb(NO_3)_2$, $NiSO_4.6H_2O$ (AR grade) (SRL chemicals) were used for preparing the 500 mg/L stock solution, using double distilled water.

2.2. *Synthesis of trihydroxy monomer*

To a three-necked round bottom flask equipped with a reflux condenser, Dean-stark trap and a magnetic stirrer, 0.1 mol 3,4-dihydroxybenzaldehyde, 0.1 mol *p*-aminophenol and 120 mL of absolute ethanol were added. To this catalytic quantity of *p*-toluenesulphonic acid 0.25 g was added. The reaction mixture was stirred at room temperature and heated in an oil bath at 90 °C for 15 min. The ethanol–water azeotrope formed was collected in the Dean-stark trap and the contents were further refluxed for 45–60 min. About 50 mL of ethanol was distilled off and the resulting mixture was again refluxed for 2 h. The monomer formed was cooled, filtered, washed several times with hot water, washed with absolute ethanol, and dried under vacuum. The structure and scheme of the monomer synthesis is shown in Fig. 1.

2.3. *Synthesis of polyurethane (PU)*

To a 250 mL flask equipped with a magnetic stirrer 0.05 mol of the trihydroxy monomer was taken in 25 mL of DMF at room temperature. To this 4,4′-methylenediisocyanate (0.05 mol) was added drop wise and the contents were stirred for one hour at room temperature. The temperature of the reaction mixture was slowly raised at 90 °C and was stirred at this temperature for 6 h. The highly viscous solution formed was poured into water with stirring. The precipitated polymer was washed with dilute HCl, hot water, ethanol, filtered and dried in vaccum. The synthetic route of polyurethane is shown in Fig. 2.