Arabian Journal of Chemistry (2015) **8**, 414–426

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Sorption studies of heavy metal ions by salicylic acid–formaldehyde–catechol terpolymeric resin: Isotherm, kinetic and thermodynamics

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Received 27 May 2012; accepted 20 March 2013
Available online 28 March 2013

KEYWORDS

Terpolymeric resin;
Ion-exchange;
Sorption;
Thermodynamics;
SEM;
Isotherm

Abstract Terpolymeric resin has been synthesized by condensing salicylic acid with catechol employing formaldehyde as a cross linking agent at 80 ± 5 °C using DMF as a solvent. The resin was characterized by elemental analysis, FTIR, XRD and thermal analysis (TGA, DTA and DTG). The morphology of the resin was studied by optical photographs and scanning electron micrographs (SEM) at different magnifications. The physico-chemical properties have been studied. The uptake behavior of various metal ions viz. Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) towards synthesized resin has been studied depending on contact time, pH and temperature. The selectivity order found is: Cu(II) > Zn(II) > Pb(II) > Ni(II) > Cd(II). The sorption data obtained at optimized conditions were analyzed by six two parameter isotherm models like Langmuir, Freundlich, Temkin, Dubinin–Radushkevich (D–R), Halsey and Harkins–Jura. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms were found better to describe the sorption data with high correlation for the adsorption with a low SSE value for all the metals under study. The adsorption capacities of the SFC resin for removal of Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) were determined with the Langmuir equation and found to be 0.815, 1.104, 1.215, 0.498, and 0.931 mmol/g respectively. The adsorption process follows first order kinetics and specific rate constant K_r was obtained by the application of Lagergren equation. Thermodynamic parameters viz. ΔG^{ads}, ΔS^{ads} and ΔH^{ads} have also been calculated for the metal-resin systems. The external diffusion rate constant (K_s) and intra-particle diffusion rate

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Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2013.03.012

constant (K_{id}) were calculated by Spahn–Schlunder and Weber–Morris models respectively. Desorption studies were done using various desorbing agents viz. de-ionized water, boiled water, various concentrations of HCl, ammonia, thiourea, citric acid and tartaric acid.

1. Introduction

Removing pollutants from wastewater is an important process and is becoming more important with increasing industrial activities. There are many incidents of extensive mortality and/or contamination of fish and other aquatic species from the discharge of heavy metal containing wastewater. The cumulative absorption of small quantities of lead into the human life causes gastrointestinal, genitourinary, musculoskeletal, hematopoetic and reproductive abnormalities and anaemia. Ingestion of large doses of zinc produces toxic symptoms viz. fever, diarrhoea and gastrointestinal tract irritation in humans. Human intact of excessively large doses of copper and nickel leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage and central nervous system irritation followed by depression (Pehlivan and Altum, 2006).

For the removal, separation and enrichment of trace metals from aqueous solutions many techniques are available such as chemical precipitation, oxidation, reduction, coagulation, adsorption, solvent extraction and ion-exchange. The extraction of metal ions using chelating ion exchange resin is a green analytical method since it does not involve the use of toxic chlorinated organic solvents, which are very frequently used in conventional liquid–liquid extraction technique or other methods (Sharma, 2001). Ion exchange is a popular method owing to its applicability to both pre-concentration and separation. The interest in this type of chelating resins is due to the rapid adsorption of metal ions, higher selectivity and less swelling in comparison to the analogous organic polymers (Liu et al., 2011).

Terpolymer resins of o-cresol-urea–formaldehyde have been prepared in the presence of acid catalyst with different molar proportions of monomers (Karunakaran and Magesh, 2011). p-Hydroxybenzoic acid has been used extensively as an analytical reagent in the determination of metal ions due to its chelating property. The synthesis of chelating resin containing p-hydroxybenzoic acid functionality is due to the preparation of insoluble functionalized polymers which can provide more flexible working conditions together with good stability and high capacity for certain metal ions. The ion-exchange resin from p-hydroxybenzoic acid, resorcinol and formaldehyde was derived and studied its ion exchange capacity and selectivity towards Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) ions (Bhatt et al., 2012). Iminodiacetic acid (IDA) containing commercial resins Amberlite IRC 748 (Zainol and Nicol, 2009) and Amberlite XAD-4 (Hosseini et al., 2006) were employed for the separation and preconcentration of transition metal ions. Some natural porous materials such as diatomite (Sheng et al., 2009) and bentonite (Yang et al., 2009) were also studied for their ion exchange properties.

The terpolymeric resin of 4-hydroxyacetophenone-oxamide-formaldehyde has been synthesized in acidic media (Gurnule et al., 2003). The chelation behavior of the phenolic-formaldehyde polymers towards the trivalent lanthanide metal ions such as La^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, and Tb^{3+} by a static batch equilibrium technique at 25 °C as a function of contact time, pH and concentration (Mubarak et al., 2004). Ion-exchange resins from the diazonium salt of aniline with phenol/resorcinol coupled with formaldehyde have been prepared alkaline medium and studied the uptake behavior of alkali and alkaline earth metal ions. The optimum conditions for effective separation of Cu^{2+} from UO_2^{2+} were also determined (Samal et al., 2000).

Resorcinol–formaldehyde resin has been evaluated for caesium removal and caesium elution characteristics (Burgeson et al., 2006). A new spherical form of resorcinol–formaldehyde resin was also tested for the efficiency of caesium removal from the complex mixture of radioisotopic liquid wastes (King et al., 2006). Resin from salicylic acid and formaldehyde with resorcinol in DMF media has also been prepared and studied for its chelation ion-exchange properties (Shah et al., 2007). Chelating ion-exchange resin from anthranilic acid and formaldehyde with resorcinol in DMF media has been synthesized and applied for the separation of transition and post transition metal ions from synthetic binary mixtures using tartaric acid as eluting agent (Shah et al., 2006). So far no resin based on salicylic acid–formaldehyde–catechol in DMF media has been reported. As industrial effluents are often rich in transition and post transition metal ions, removal and recovery of these metals is an important task for industries.

2. Experimental procedure

2.1. Materials and reagents

Analytical grade chemicals such as salicylic acid, formaldehyde (37%) and catechol were purchased from Qualigens fine chemicals, Mumbai and used as received without further purification. Solutions of acids and alkalies were prepared by dissolving appropriate amount of the particular compound in double distilled water and standardized by the literature methods (Vogel, 1989). Stock solutions of metal salts under study were prepared by dissolving appropriate amount of analytical reagent grade metal acetates in double distilled water. The stock solutions were further diluted with double distilled water to desire concentration for obtaining test solutions. Glassware were cleaned by overnight soaking in chromic acid followed by multiple rinsing with water. All the other reagents used were of analytical grade and were used as such. Double distilled and deionized water was used throughout the research work. All pH measurements were carried out with digital pH meter (Elico CL-44) equipped with a combined glass/calomel electrode. A Perkin-Elmer Model 5000 atomic absorption spectrometer (Perkin-Elmer, Shelton, CT-USA) fitted with nickel, copper, zinc, cadmium and lead hollow cathode lamps was used to analyze the concentration of these heavy metals under study. Three standard solutions with concentration of heavy metal ions in the linear range of the instrument were