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ORIGINAL ARTICLE

Heavy and toxic metal uptake by mesoporous hypercrosslinked SMA beads: Isotherms and kinetics

Renuka Gonte [a], **K. Balasubramanian** [b,*]

[a] *Department of Applied Chemistry, Defence Institute of Advanced Technology, Girinagar, Pune 411 025, India*
[b] *Department of Materials Engineering, Defence Institute of Advanced Technology, Girinagar, Pune 411 025, India*

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Abstract Hypercrosslinked styrene-maleic acid copolymer beads were used for the removal of metal ions from mimicked industrial effluents. The polymer was characterized by SEM which revealed the presence of a porous network. Carboxyl acid groups of the polymer were identified as active sites for metal uptake. Highly porous surface enhanced metal ion uptake was achieved through a physicochemical process. Equilibrium sorption of metal ions was best described by the Freundlich and Temkin model with $R^2 > 0.99$. Adsorption followed pseudo first and pseudo second order reaction kinetics. Intraparticle diffusion model suggested a three step equilibrium. Desorption was a fast process with ~90% in 60 min.

1. Introduction

In recent years we have experienced an increasing awareness about water pollution and its far reaching effects have prompted concerted efforts toward pollution abatement (Dönmez et al., 1999). Rapid industrialization has seriously contributed to the release of toxic heavy metals in water streams. Mining, electroplating, metal processing, textile and battery manufacturing industries are the main sources of heavy metal contamination (Babel and Opiso, 2007; Nwuche and Ugoji, 2008). These activities pollute water streams especially rivers and make them lose their potential value and beneficial uses (Celik and Demirbas, 2005; Demirbas et al., 2005; Kadirvelu et al., 2001). Contamination of aqueous environments by heavy metals and dyes is a worldwide environmental problem due to their toxic effects and accumulation through the food chain (Kapoor et al., 1999; Perez-Rama et al., 2002; Sternberg and Dorn, 2002). Among these heavy metal ions, the ions of Cd, Zn, Hg, Pb, Cr, Cu, As etc. have gained importance due to their highly toxic nature even at very low concentrations. High concentration of heavy metals in the environment can be detrimental to a variety of living species. Excessive ingestion of these metals by humans can cause accumulative poisoning, cancer, nervous system damage and ultimately death (Corapcioglu and Huang, 1987; Issabayeva et al., 2007). Heavy metals cannot be metabolized and bioaccumulate in the body of organisms. These toxic metals can move through the biological chain thereby reaching the human being and leading to chronic and acute ailments. Heavy metal toxicity can result in damaged or reduced mental and central nervous functions,

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[*] Corresponding author. Tel.: +91 2024304207.
E-mail address: balask@diat.ac.in (K. Balasubramanian).

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lower energy levels and damage to the blood composition, lungs, kidneys, liver and organs (Volesky and Holan, 1995; Zulkali et al., 2006).

Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts and chocolate. The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper and paper board mills, wood pulp production and the fertilizer industry (Nuhoglu and Oguz, 2003; Wan Ngah et al., 2002; Ozsoy and Kumbur, 2006). Excessive intake of copper results in accumulation in the liver, leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, and central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney, hemolysis, liver and kidney damage, irritation of upper respiratory tract, gastrointestinal disturbance, and diarrhea It is also toxic to aquatic organisms even at very small concentrations in natural water (Ozsoy and Kumbur, 2006). Zinc is biologically essential but an overdose can lead to depression, lethargy, and neurologic signs such as seizures and ataxia and increased thirst (Kurniawan et al., 2006). Zinc is harmful for both irrigational and industrial applications. Zinc is introduced into water from metal mining, melting, plating, pesticides, oil-based paint pigments, alloy processing and sewage sludge. The most common adverse health effect of nickel in humans is an allergic reaction; large amounts of nickel can cause lung and nasal sinus cancers. Nickel (Ni) may be found in wastewater discharges from mining, electroplating, pigments and ceramic industries, and battery and accumulator manufacturing (Parab et al., 2006). Nickel is toxic to a variety of aquatic organisms, even at very low concentrations. The most common adverse health effect of nickel in humans is an allergic reaction; large amounts of nickel can cause lung cancer and nasal sinus cancers. Impact of Ni can be manifested in chronic toxicity, dermatitis, nausea, chronic asthma abdominal cramps, diarrhea, vertigo and lassitude but acute toxicity is not typical (Borbély and Nagy, 2009). Nickel is also toxic, especially to activated sludge bacteria. The presence of Ni(II) is detrimental to the operation of anaerobic digesters used in wastewater treatment plants. Thus removal of trace amounts of heavy metal ions from wastewater and drinking water is of great importance due to its high toxicity (Abdel-Ghani and Elchaghaby, 2007; Abdel-Ghani et al., 2009; Resmi et al., 2010).

Current methods for wastewater treatment include precipitation, coagulation/flotation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, biological process, chemical reactions, adsorption and ion exchange. But the selection of the wastewater treatment method is based on the concentration of waste and the cost of treatment. However, these processes have significant disadvantages such as incomplete metal removal, particularly at low concentrations and high operational costs (Cochrane et al., 2006). Cost-effective treatment technologies, therefore, are needed to meet these requirements. Out of the several physicochemical processes for the removal and recovery of metal ions from effluents, adsorption is the most effective one (Nyholm et al., 1992; Mavros et al., 1994; Ghosh and Bhattacharyya, 2002). The important aspect of the adsorption process is easy regeneration ability and less operational cost, simple design, easy operation and free or less generation of toxic substances (Khan et al., 2008). Adsorption techniques have proven successful in removing colored organic species and the choice of the adsorbent is one of the key factors determining the effectiveness of any adsorption process. The adsorption process at solid/liquid interface has been extensively employed for several reasons, mainly due to its efficiency and economy (Namasivayam et al., 2003; Gürses et al., 2006). Physical adsorption because of its low cost, high efficiency, easy handling, wide variety of adsorbents and high stabilities toward the adsorbents, has become the most widely used methods for the elimination of dye from wastewater.

Porous materials such as clay (Jaber et al., 2005), activated carbon (Zhu et al., 2009), zeolites (Wingenfelder et al., 2009) and biomass (Deng and Ting, 2005) are usually used as toxic metal ion adsorbents because of their high surface area, large pore volume, and the presence of exchangeable ions presenting themselves as good candidates for adsorbents. For better adsorption performance, the pore size of a porous adsorbent should match the adsorbates atomic/molecular size (Yang, 2003). Compared to traditional microporous adsorbents such as activated carbons and zeolites, organic porous polymers possess various advantages like pore size tuning (Jiang et al., 2007, 2008). Introduction of a specific surface functionality can introduce a wide variety of synthetic strategies and enhance adsorption properties (Karbarz et al., 2010). Further these polymers can be replicated from well-defined monomers and optimized conditions (Carrington et al., 2007; Balaji et al., 2006; Adanur, 2001). These advantages render microporous polymers to be potential and possibly superior candidates for the removal of toxic metal ions from wastewater. Hypercrosslinked polymers represent a class of predominantly microporous organic materials that can exhibit high surface area (Tsyurupa et al., 2003) and are also being evaluated as potential candidates for hydrogen and methane storage (Wood et al., 2007, 2008; Lee et al., 2006). Macroporous or mesoporous analogous materials have been widely reported as adsorbents for organic/gas adsorbates and commercial microporous hypercrosslinked polymers with the functional group as a strong acid cation-exchange resin which has accelerated the development of several important technologies such as purification, removal of hazardous organic materials and so on.

In the present study, the equilibrium adsorption of Cu(II), Ni(II), Zn(II) and Co(II) ions onto hypercrosslinked styrene-maleic acid copolymer (SMA) beads from mimicked wastewater systems was investigated. The influence of experimental conditions such as pH, adsorbent dose, initial metal and ion concentration was investigated. The Langmuir, Freundlich, Temkin and D–R equations were used to fit the equilibrium isotherm. Adsorption rates were determined quantitatively and compared by the first and second-order kinetic models. The mechanism and thermodynamics of adsorption were also studied. This information can be useful for system design in the industrial waste water treatment plants.

2. Materials and methods

2.1. Materials

Styrene (Merk, India) and divinylbenzene (Sigma Aldrich 80%, India) were purified with 1N NaOH prior to use. Azobisisobutyronitrile (AIBN, SAS, India) and maleic anhydride (Fluka, India) were recrystallized from chloroform. Methyl isobutyl ketone, NaOH, NaCl, $Mg(OH)_2$, zinc acetate, copper sulfate pentahydrate, cobalt chloride heptahydrate and nickel