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Equilibrium and kinetic behavior on cadmium and lead removal by using synthetic polymer

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ABSTRACT

It is known that synthetic polymer plays a big role in various applications. One of its potentials is to remove heavy metal ions through single batch adsorption. Adsorption behavior and mechanism of synthetic polymer are the two main focuses in this research. The synthetic polymer of Poly(AN-*co*-AA) has been successfully polymerized, modified with hydroxylamine hydrochloride and removed Cd^{2+} and Pb^{2+}. The poly(AN-*co*-AA) and amidoxime (AO) modified poly(AN-*co*-AA) were characterized by Fourier Transform Infrared Analysis (FTIR), microanalysis, Scanning Electron Microscopy (SEM) and Thermogravimetry (TGA). At pH 9, the percentage removal for Cd^{2+} (90%) and Pb^{2+} (98%) were the highest with adsorbent dosage at 4 gL^{-1} and 8 $g\,L^{-1}$, respectively. The experimental data for Cd^{2+} (20 $mg\,g^{-1}$) and Pb^{2+} (125 $mg\,g^{-1}$) were fitted well by Sips and Freundlich isotherms model, respectively. The adsorption rate for both Cd^{2+} and Pb^{2+} were stated by using Lagergren pseudo-first order.

1. Introduction

Water contamination could lead to a serious problem due to the generation of toxic compounds from industrial activities [1]. The untreated industrial effluents may lead to huge disasters in the ecosystem in a long run and the worst impact will be faced by future generations. Therefore, they need to be treated before being released into the streams. Heavy metal ions from the industry create a big concern in public due to their toxicity that can affect global health [2]. The toxic heavy metal ions are usually found in wastewater from mining ore processing, paint, chemicals and fertilizer industries [3]. Most of the heavy metal elements such as arsenic, cadmium, lead and mercury are very toxic, even in low concentration [4]. The heavy metals of cadmium (Cd) and lead (Pb) were categorized as high toxic heavy metals compared to some heavy metals like zinc, copper and manganese that required for living organism but in low concentrations. The Cd and Pb also were widely produced as effluent waste in variety of industrial sectors. Malaysia Third Schedule Environmental Quality Act, 1974 has stipulated that Cd and Pb were among heavy metals that was permitted to presence at low concentration in industrial discharge wastewater.

Electroplating and metal surface treatment processes generate significant quantities of wastewaters containing heavy metals, such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium, from a variety of applications. These include electroplating, electroless depositions, conversion-coating, anodizing-cleaning, milling, and etching [5]. Wastewater from electroplating operations is classified into in four categories: water rinsing, spent plating solutions, uncontaminated water from equipment cooling, and water from washing equipment and containers, and for wet cleanup of the plant [6]. The rinsing of material after plating operation is required to remove any plating bath solution that may be left on the material. Concentrated wastewater consists of spending plating solutions for the baths. Rinsing operation emanates the largest volume of wastewater from metal plating operations. Rinse waters finally become contaminated with varying concentration of heavy metals as per the type of

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rinsing scheme. For instance, chemical compositions of the plating baths used in Hong Kong and India were reported to consist of high concentrations of copper and cadmium, ranged between 8 and 14 g/L [7,8].

Heavy metals could cause acute or chronic diseases to human being. Water containing 0.5 mg/l or more chromium is considered highly toxic because it has carcinogenic and mutagenic properties. Cd^{2+}, for example, could lead to proteinuria, lung cancer and osteomalacia while Pb^{2+} could cause encephalopathy, anemia, abdominal pain, nephropathy and foot or wrist drop [9]. The heavy metal can be treated through several methods such as sedimentation, flocculation, adsorption, co-precipitation, cation and anion exchanger, microbial activity and plant uptake. Zhang et al. [10] studied the adsorption of Cd^{2+} and Pb^{2+} onto ethylenediaminetetraacetic dianhydride (EDTAD)-modified magnetic baker's yeast biomass (EMB). The results showed that the maximum adsorption capacities (q_m) of Pb^{2+} and Cd^{2+} were 99 mg g^{-1} and 49 mg g^{-1} respectively. Sonmezay et al. [11] investigated the ability of manganoxide minerals to capture Cd^{2+} and Pb^{2+} with q_m were 98 mg g^{-1} and 7 mg g^{-1} for Pb^{2+} and Cd^{2+} respectively. The adsorption properties of amino-functionalized, mercapto-functionalized and carboxylic-functionalized towards Cd^{2+} and Pb^{2+} were also reported [12]. Other reported adsorbents including: *Bauhinia purpurea* pods [13], chitosan [14], bagasse [15], cucumis melopeel activated carbon [16], doum palm shell [17] and magnetic acid-treated activated carbon nanocomposite [18].

This work focuses on the removal of heavy metal toxicity of cadmium (Cd^{2+}) and lead (Pb^{2+}) using an adsorption process. Adsorption is a process where certain concentration of adsorbate is adsorbed on the adsorbent surface. Amidoxime (AO) modified poly (acrylonitrile-*co*-acrylic acid) (poly(AN-*co*-AA)) was prepared in this work as the adsorbent for Cd^{2+} and Pb^{2+}. The type of polymer was chosen due to the existence of unique functional group to attract Cd^{2+} and Pb^{2+} and the result was promising. The reactive cyano group (C≡N) presents in acrylonitrile (AN) could be converted into a unique particular functional groups. The high nitrile–nitrile dipolar interaction in AN resulted in low moisture absorption and causes hydrophobicity. Thus, the lack of active functionality was overcome by incorporating acrylic acid (AA) as co-monomer. In addition, AA promotes strong adhesive properties for modification of poly(AN-*co*-AA). The hydroxylamine hydrochloride was chosen in this work as a modification agent due to capability of amidoxime (AO) group to form complex attachment with heavy metal ions [19]. The conversion of nitrile groups into the AO group will enhance the metal concentration sorption ability of the poly(AN-*co*-AA). Thus, every functional group in this polymer chain plays an important role in attracting and adsorbing the heavy metals. Fig. 1 displays the attraction of the AO modified poly(AN-*co*-AA) with the heavy metal ions (positive charge) in a square planar formation.

The proposed formation is possible due to the affinity of the functional group in AO modified poly(AN-*co*-AA) towards the heavy metal ion [20]. The AO modified poly(AN-*co*-AA) attracted heavy metal ions through the functional group of nitro (NO) and amine (NH_2). The NO group formed a dative covalent bond and NH_2 group formed van der Waals forces towards heavy metal ions. The AO containing adsorbents is also environmentally friendly material due to its versatility in regeneration and can be reused in heavy metal uptake process [21,22]. Ge et al. reported reusability of amidoxime (AO) chelatin resin through five consecutive adsorption and desorption cycles, which has reduce break-through capacity of 85% for Pb^{2+}. Sihn et al. studied amidoxime (AO) polymer of intrinsic microporosity (PIM-1) that was capable for regeneration and more than 92% of Uranium (U) can be obtained in three cycles [23]. The objective of this paper is to remove heavy metal ions (Cd^{2+} and Pb^{2+}) by using AO modified poly(AN-*co*-AA) from aqueous solution. In addition, the study of the adsorption behavior of Cd^{2+} and Pb^{2+} onto AO modified poly(AN-*co*-AA) was carried out through equilibrium isotherms and kinetic models.

2. Materials and methods

2.1. Poly(AN-co-AA) synthesis

Redox polymerizations were performed at 40 °C under nitrogen (N_2) gas. The acrylonitrile (R & M Chemical, Essex, UK), acrylic acid (MERCK, Darmstadt, Germany), sodium bisulphate (Systerm ChemAR, Malaysia) and potassium persulphate (Systerm ChemAR, Malaysia) were added into deionized water in a round bottom flask. After 3 h, the polymer formed was allowed to precipitate in methanol for 1 h. Then, the polymer was washed successively with methanol and deionized water, filtered and dried [24]. The 3 h time of redox polymerization at low temperature (40 °C) can be considered as energy saving and efficient preparation method as.

2.2. Amidoxime modification of poly(AN-co-AA)

The hydroxylamine hydrochloride (Systerm ChemAR, Shah Alam, Malaysia) was adjusted to pH 6 with sodium bicarbonate and was later heated continuously at a constant temperature of 70 °C. The poly(AN-*co*-AA) was then added into the hydroxylamine hydrochloride solution and allowed to react for 1hr. Consequently, the AO modified poly(AN-*co*-AA) formed was filtered, washed and dried [24].

2.3. Batch adsorption

Batch adsorption was carried out using 150 ml Erlenmeyer flask containing 50 ml of Cd^{2+} solution from cadmium nitrate-tetrahydrate (R & M Chemical, Essex, UK). The adsorbent dosage was 2 g L^{-1} of AO modified poly(AN-*co*-AA). The solution was then stirred for 90 min for 150 rpm at a room temperature of 25 °C. The solution was tested with

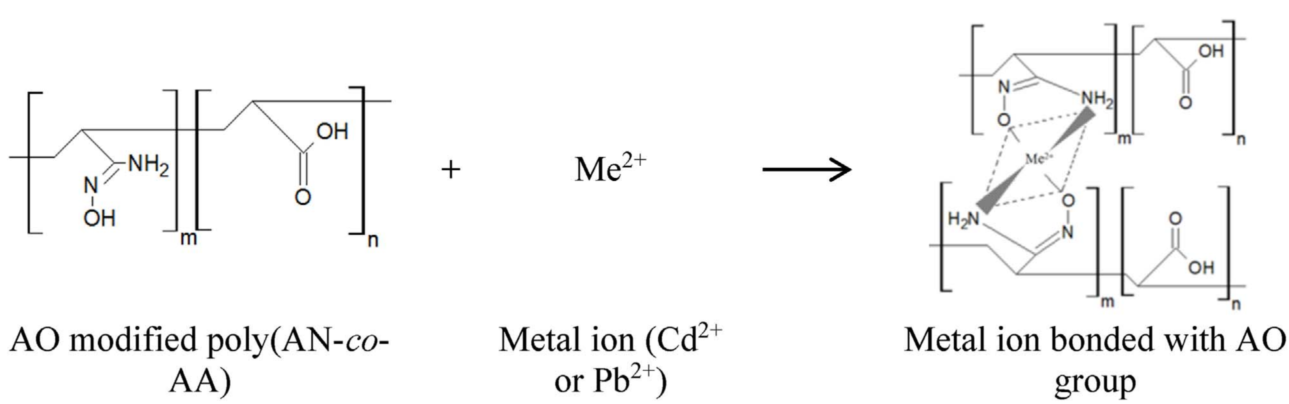

Fig. 1. Reaction of amidoxime (AO) modified poly(AN-*co*-AA) reacted with metal ion in aqueous solution, producing metal ion bonded with amidoxime (AO) group.