Studies on interference of adsorption of heavy metal ions on chelating sorbents from cassava and Amidoxime-modified Polyacrylonitrile-grafted-Cassava Starch

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ABSTRACT

Polyacrylonitrile (PAN) is ideal polymeric matrix for adsorption due to its tolerance to most solvents, thermal stability and abrasion resistance. In this study, active nitrile group was converted into amidoxime functional group to form a chelating sorbent. Cassava starch (CS) that contains hydroxyl moiety is well known as effective biosorbent for the removal of heavy metal ions in aqueous solution. Batch adsorption was performed to study the interference of adsorption of heavy metal ions on the chelating sorbents prepared from cassava and Amidoxime-modified Polyacrylonitrile-grafted-Cassava Starch. It was found that the removal efficiencies of amidoxime-modified poly(AN-g-CS) towards Cu(II) ions was 43%, whilst the removal efficiencies towards Cr(III) and As(III) were 47% and 29% respectively. It was also shown that the presence of binary and ternary ions concentration greatly affects the sorption capacities of the adsorbents. The sorption capacities of the heavy metal ions was in the order As<Cu<Cr. The presence of Cr^{3+} reduced the removal efficiency of Cu^{2+} from 56.02mg/g to 25.89mg/g (46%), while As^{3+} reduced it to 24.32mg/g (43%). In a Ternary system, Cr^{3+} and As^{3+} jointly reduced the removal of Cu^{2+} to 22.56mg/g (40%). This study demonstrates that amidoxime-modified poly(AN-g-CS) has potential to be applied as good adsorbent to remove heavy metal ions from aqueous solution but interference by co-metals is noteworthy.

Keywords: cassava starch; amidoxime; graft copolymerization; heavy metal ions, hydroxylamine hydrochloride; oxime group; polyacrylonitrile.

INTRODUCTION

Global industrialization has resulted in introduction of metal contaminants into the environment and this is of concern because of the serious effects to animals and plants[1]. Some of the poisonous heavy metal ions that are persistent and cause serious health challenges include chromium, mercury, nickel, copper, zinc, lead and cadmium [2,3]. Although certain amount of zinc intake is considered necessary and very vital for physiological activities in the human body by stabilizing several biological processes, excessive intake of zinc into human body leads to severe stomach pains, skin rashes, vomiting, weakness of the body and anaemia[4]. Copper is one of the most important elements in the human body, however, if ingested above the threshold limit can result in convulsion, vomiting, cramps and eventually death[5].

Metal removal by Chemical precipitation, ion exchange, surface complexation, filtration and electrode deposition are limited by high cost of chemicals, metal selectivity; low adsorption capacity and low potential for regeneration[5]. Adsorption is regarded as one of the most vital techniques due to availability of raw materials, simplicity with sufficient adsorption of heavy metal ions[7].

Attention of many researchers has been drawn towards the use of polyacrylonitrile PAN for adsorption of heavy metal ions in industries due to its special features that include hardness and flexibility, chemical resistance, consistency with other polar materials, permeability[7]and the existence of nitrile functional groups along polymer chains that could be converted into another functional groups[8]. Hence, PAN performance has been improved *via* chemical modification with various reagents such as hydroxylamine, ethylenediamine, hydrazine, thioamide and imidazoline to develop new moieties that are vital for the removal of cationic metal ions in wastewater[9,10].

Agricultural adsorbent is low-cost, cheap and abundant in nature that requires little processing. Plant wastes are considered as inexpensive as they have no or very low economic value[11,12]. Many adsorption studies have focused on untreated plant wastes such as papaya wood[13], maize leaf[14], leaf powder[15], peanut hull pellets[16], rice husk ash and neem bark[17]. Some of the advantages of using plant waste for wastewater treatment include simple technique, good adsorption capacity, abundant availability, selective adsorption of heavy metal ions, easy regeneration, low cost and requires little processing [18,19]. It was reported that metal ions binding by lignocellulosic biosorbents occurred through moieties such as carboxyl or phenolics[20]. Metal biosorption is a complex process involving chemisorption, complextion, adsorption-complexation of surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface and surface adsorption [21,22].

In the present work, we investigated the synergistic effect of CS biosorbent and PAN to make heavy metal ions adsorption in aqueous solution. Cassava starch (CS) was incorporated into hydrophobic polyacrylonitrile (PAN) system to weaken the nitrile-nitrile dipolar interaction that hindered cyano groups to be accessible by any reagent. The cyano functional group in poly(AN-grafted *(g)*-CS) was utilized to be converted into desired chelating group (oxime) to form amidoxime-modified poly(AN-*g*-CS). The chemically modified poly(AN-*g*-CS) was expected to make heavy metal ions capture *via* complex formation of 'polymer-metal ions'. The CS consists of lignocellulosics that are hygroscopic and has an affinity for water. Hence, it is expected that the amidoxime-modified poly(AN-*g*-CS) could absorb high capacities of heavy metal ions from aqueous solution[20].

MATERIALS AND METHODS

The reagents used for the polymerization was acrylonitrile (99% grade) supplied by Merck Co. (United Kingdom) and cassava starch was obtained from the local market in Selangor, Malaysia where the study was carried out. Potassium persulphate (KPS) and sodium bisulfite (SBS) were supplied by Systerm (Malaysia). Hydroxylamine hydrochloride (Acros organics, USA) was used for chemical modification. Sodium hydroxide (analytical grade) was supplied by R & M (U.K). Methanol (analytical grade) was supplied by ChemPur Systerm (Malaysia). Acrylonitrile was purified by passing the monomer through a short column of neutral alumina (grade for chromatography). All other reagents were used as received.

Synthesis and characterization

The preparation of poly(AN-*g*-CS) has been reported in previous study[23]. Cassava starch (CS) was initially peeled and washed thoroughly with deionised water to remove the surface impurities. It was dried under the sunlight for about 48 h before further drying in a vacuum oven at 50 ℃ overnight to eliminate the moisture. The particle size of CS was reduced by mortar mill and was sieved to obtain a desirable size of about 10 μm. The final product was stored in a desiccator for further use.

20 g of dried CS and 200 mL of deionized water were mixed in a three neck round bottom flask fitted with a water condenser under nitrogen atmosphere. The mixture was stirred for 1 h to form cassava slurry. The acrylonitrile (AN) (15 mL, 13.3 g) was added into the reaction medium, followed by SBS (2.09 g, 0.27mol.L^{-1}) and KPS (2.16 g, 0.44 mol.L^{-1}). The graft copolymerization of poly(AN-g-CS) (ratio of AN:CS was 1:3) was performed at different condition parameters. The reaction temperature was varied to 40℃, 50℃ and 60℃ under constant stirring at 250 rpm. The reaction was terminated by pouring the product into 50 mL of methanol and left to precipitate for 1 h. The grafted copolymer was then filtered and washed successfully with 50 mL of methanol and 100 mL of deionized water. The polymer was dried in a vacuum oven at 50 ℃ until a constant weight was obtained.

The removal of the homopolyacrylonitrile (homoPAN) from poly(AN-*g*-CS) was accomplished by stirring the poly(AN-*g*-CS) at 200 rpm in 25 mL of dimethyl sulfoxide (DMSO) for 24 h to dissolve the homoPAN. The poly(AN-*g*-CS) was filtered and washed successfully with 50 mL of methanol and 100 mL of deionized water. The purified poly(AN-*g*-CS) was dried in a vacuum oven at 50℃ until a constant weight was obtained [23].

Modification of poly(AN-g-CS) with hydroxylamine hydrochloride,

The chemical modification of poly(AN-g-CS) with hydroxylamine hydrochloride to form amidoxime-modified poly(AN-*g*-CS) has been reported previously[23]. 2 g of poly(AN-*g*-CS), 25 mL of methanol and 3 g of hydroxylamine hydrochloride ($NH_2OH.HCl$) were added into a 250 mL three-neck round-bottom flask that was fitted with a reflux condenser. The mixture was stirred at room temperature for 2 h. 6 mL of sodium hydroxide solution (1 M) was added to the reaction mixture to neutralize the hydrochloric acid (HCl). The pH of the mixture was adjusted to pH 8. The reaction was allowed to proceed for 6 h at 70 °C under constant stirring. The amidoxime-modified poly(AN-*g*-CS) was filtered and washed with 50 mL of ethanol and 100 mL of deionized water. The polymer was dried in a vacuum oven at 50 °C till a constant weight was obtained[7].

Batch Adsorption

Batch experiment was performed at room temperature in order to establish the sorption capacity towards single-metal ion by mixing 0.10 g of the sorbent with 100 mL of heavy metal ion solution in a 250 mL conical flask. The mixture was magnetically stirred at 200 rpm for 2 h. 5 mL of sample was withdrawn from the bulk solution and filtered using membrane filter. The initial and final concentration of metal ions was then analyzed using atomic absorption spectrometer, S series air pump, (U.S.A).

RESULTS AND DISCUSSION

Interference studies

The adsorption interference of specific heavy metal ions in amidoxime modified poly(AN-*g*-CS) adsorption from mixture of Cu(II), Cr(III) and As(III) were studied. The concentration of each heavy metal ion solution was fixed to 100 $mg.L^{-1}$; contact time was 2 hours with 0.1 g of sorbent dosage. Table 1 shows the sorption capacities of CS, poly(AN-*g*-CS) and amidoxime modified poly(AN-*g*-CS) in the presence of co-ions. It was shown that the presence binary and ternary ions concentration greatly affects the sorption capacities of all the adsorbents. The sorption capacities of the heavy metal ions increased in the order As<Cu< Cr. This sequence might be due to the influence of ionic potential and ionic radius. Similar observation was published by Jaber[24]; the maximum amount of heavy metal ions increased in the order Zn<Cd<Cu. Among the heavy metal ions, chromium has the highest ionic potential (3.0) as compared to the ionic potential of copper (2.59) and arsenic (1.67). However, the ionic radii of Cr^{3+}, Cu^{2+} and Ar^{3+} were found to be 0.061 nm, 0.47 nm and 0.47 nm respectively[25]. Chromium with the smallest ionic radius can easily penetrate through the smaller pores; hence, form larger access into the adsorbent surface. The presence of Cr^{3+} reduced the removal efficiency of Cu^{2+} from 56.02mg/g to 25.89mg/g (46%), while As^{3+} reduced it to 24.32mg/g (43%). In a Ternary system, Cr^{3+} and As^{3+} jointly reduced the removal of Cu^{2+} to 22.56mg/g (40%). This study demonstrates that amidoxime-modified poly(AN-*g*-CS) has potential to be applied as good adsorbent to remove heavy metal ions from aqueous solution but interference by co-metals is a major factor for consideration

Table 1: interference studies of the heavy metal ions using amidoxime-modified poly(AN-*g*-CS) as adsorbent.

	Removal efficiency ($mg.g^{-1}$)		
	Cu^{2+}	Cr^{3+}	As^{3+}
Single metal ion Cu^{2+}	56.02		
Binary system Cu^{2+}/ Cr^{3+}	25.89	29.67	
Cu^{2+}/ As^{3+}	24.32		4.68
Ternary system Cu^{2+}/Cr^{3+}/ As^{3+}	22.56	26.92	3.41

Application studies using industrial effluents

Industrial effluent containing Cu(II), Cr(III) and As(III) were collected from industrial effluent waste in Malaysia with initial concentration of 137 ppm, 150 ppm and 125 ppm respectively. As shown in Table 2, application study was carried out with the heavy metal ions that were adsorbed onto CS, poly(AN-*g*-CS) and amidoxime-modified poly(AN-*g*-CS) to investigate the applicability of the materials to remove heavy metal ions in real application (industrial effluent). Batch adsorption studies were carried out similar to the batch adsorption studies using synthetic sample. Amidoximed-modified poly(AN-*g*-CS) showed better removal efficiency of 9.16 $mg.g^{-1}$ of Cu(II), 9.13 $mg.g^{-1}$ of Cr(III) and 5.14 $mg.g^{-1}$ of As(III) as compared with 0.93 $mg.g^{-1}$ Cu(II), 0.82 $mg.g^{-1}$ Cr(III) and 0.18 $mg.g^{-1}$ As(III) of poly(AN-g-CS), while for CS, 0.93 $mg.g^{-1}$ Cu(II), 0.65 $mg.g^{-1}$ Cr(III) and 0.17 $mg.g^{-1}$ As(III). With this results, it is expected that amidoximed-modified poly(AN-*g*-CS) has potential to be selected as alternative for industries in the removal of heavy metal ions in industrial waste.

Table 2 Application studies of adsorption of CS, poly(AN-g-CS) and amidoxime-modified poly(AN-g-CS) towards water effluent containing Cu(II) ions, Cr(III) ions and As(III) ions.

Adsorbents	Removal efficiency (%)		
	Cu(II) ions	Cr(III) ions	As(III) ions
Amidoxime-modified poly(AN-g-CS)	9.16	9.13	5.14
Poly(AN-g-CS)	0.93	0.82	0.18
CS	0.93	0.65	0.17

CONCLUSION

This study demonstrates that amidoxime-modified poly(AN-*g*-CS) has potential to be applied as good adsorbent to remove heavy metal ions from aqueous solution but interference by co-metals is a major factor for consideration in its application.

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