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Equilibrium, kinetic, thermodynamic and desorption studies of cadmium and lead by polyaniline grafted cross-linked chitosan beads from aqueous solution

E. Igberase *, P. Osifo

Department of Chemical Engineering, Vaal University of Technology, Private Mail Bag X021, Vanderbijlpark 1900, South Africa

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ABSTRACT

Modification of chitosan beads by cross-linking and grafting was investigated in this work, in order to use the grafted beads in the removal of cadmium and lead from contaminated water. The beads were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM) to provide evidence of successful cross-linking and grafting. Batch experiments were carried out as a function of adsorption parameters such as pH, initial concentration, contact time and adsorbent dosage. Equilibrium data were obtained from the adsorption experiment performed, the data were correlated with the Langmuir and Freundlich isotherm models. The maximum adsorption capacity for cadmium and lead ions at a temperature of 45 °C from Langmuir model was found to be 145 mg/g and 114 mg/g respectively. Subsequently, thermodynamic parameters such as Gibb's free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) were calculated and the results showed that the adsorption of cadmium and lead ions onto polyaniline grafted cross-linked chitosan beads (GXCS) is spontaneous and endothermic in nature. The pseudo-first-order and pseudo-second-order model were used in analyzing kinetic data for both metal ions. The data fit well with the pseudo-second-order model. Desorption of GXCS loaded with cadmium and lead ions was assessed for five consecutive adsorption/desorption cycle. However, among the eluents that was investigated 0.5 M HCl was successfully used in desorbing the spent adsorbent and a percentage desorption of 98.94% and 97.50% was obtained for cadmium and lead ions respectively, at a desorption time of 3 h.

Introduction

In the past decades, water contamination by heavy metal ions has been an issue affecting the environment. The major sources of these heavy metals are the ever increasing industries that produce various kinds of physical and chemical pollutants that make their way into the river. Increasing concentrations of these metals in water tend to pose health hazard due to the fact that they are unbiodegradable [1]. For example, cadmium which causes the following health hazards: renal damage, tai-tai, hypertension, emphysema and testicular atrophy is produced by industries such as mining, smelting, metal plating, batteries and phosphate industries [2,3]. Lead on the other hand which causes health hazards such as anaemia, brain damage, dysfunction of the kidneys and the liver, infertility and abnormalities in pregnancy [4,5] is produced by industries such as paints, battery, exhaust, insecticides, plastics, water pipes, food, beverages, ointment and medicinal concoctions for flavoring and sweetening. The maximum allowable limit for cadmium and lead as given by the United States Environmental Protection Agency (USEPA) is 0.005 and 0.05 mg/l respectively.

Due to strict legislation on the discharge of these harmful metals in water bodies, it becomes important to develop various technologies that will remove or reduce these pollutants to its allowable limit. Techniques such as chemical precipitation, membrane separation, ion exchange and electrolysis have been used in the past for the removal of metal ions. However, recent studies have shown adsorption to be the most promising technique for metal ions removal due to convenience, easy operation, simplicity of design, can remove different type of pollutants and can be regenerated by some desorption process [6,7]. Ali et al. [8] stated that adsorption technique is capable of removing up to 99.9% of pollutant from wastewater.

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* Corresponding author. Tel.: +27784290538.
E-mail address: mychoice2009@yahoo.com (E. Igberase).

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Among the various adsorptive materials, chitosan has proven to be an efficient adsorbent, owning to its unique characteristics such as antimicrobial activity, biocompatibility, non-toxicity, and low cost [9]. Chitosan is a derivative of N-deacetylation of chitin, a naturally occurring polysaccharide obtained from crustaceans i.e. shrimps and crabs, and fungal biomass [10]. The presence of amine and hydroxyl group in the backbone of chitosan gives the polymer its high binding capacity in adsorption processes. Chitosan can remove metal ion concentration to near zero concentration [11]. Chitosan versatility allows the polymer to be easily modified in an attempt to change or enhance the properties of chitosan in adsorption. Modification of chitosan by cross-linking renders the polymer insoluble in acidic media, thereby increasing its mechanical and chemical stability. This method has been found by other researchers to have negative effect on adsorption capacity, due to the fact that the amine group of chitosan is involve in the cross-linking reaction [12], hence grafting of the cross-linked beads becomes important to improve the target metal adsorption properties [13].

This study reports the use polyaniline graft cross-linked chitosan beads for the removal of cadmium and lead from aqueous solution. Since amine functional group that is capable of adsorbing metal ions is present in polyanilne, it is however necessary to develop an adsorbent that will adsorb metal ions much better than any other chitosan based materials. On this note, chitosan beads were cross linked with glutaraldehyde and then grafted with polyaniline. The beads were characterized using scanning electron microscope (SEM) and X-ray diffraction (XRD). The effect of pH, adsorbent dosage, initial concentration, contact time on the adsorption of cadmium and lead were investigated. The Langmuir and Freundlich models were used to describe equilibrium isotherms for the adsorption of cadmium and lead onto GXCS. Thermodynamics of adsorption of both metal ions onto GXCS was described by parameters such as standard Gibb's free energy change (ΔG^o), standard enthalpy change (ΔH^o), and standard entropy change (ΔS^o) while the pseudo first-order and pseudo second-order kinetic model was used to describe kinetic data for GXCS. Desorption studies was carried out to evaluate the reusability of the loaded GXCS in an attempt to minimize cost.

Experimental

Materials

The chitosan flakes with average molecular weight 400 kDa and a degree of deacetylation of 74% was obtained from Labchem. Aniline (99.5%, extra pure) was purchased from AEC Amersham (Pty) Ltd. Ammonium persulfate (>98%), ethanol (>99%), hydrochloric acid (99%), 1-methyl-2-pyrrolidinone (>99%), sodium hydroxide (>99%), acetic acid (>99%), glutaraldehyde and ethylenediaminetetra-acetic acid (EDTA) were all purchased from Sigma–Aldrich. Distilled water was produced with a pure water distiller (Ultima 888 water distiller) and as used in the preparation of all solutions. The pH of the solution was measured with a pH meter (Hanna HI 8421), purchased from Sigma–Aldrich.

A shaker (labcon incubator) was used for adsorption studies carried out and a shaking speed of 120 rpm was maintained. Atomic adsorption spectrophotometer (Varian SpectrAA-10), was used to determine the amount of cadmium and lead ions adsorbed.

Adsorbate preparation

The stock solution of Cd^{2+} and Pb^{2+} was prepared by separately dissolving required amount of cadmium chloride ($CdCl_2$) and lead nitrate ($Pb(NO_3)_2$) in distilled water. The stock solution was further diluted with distilled water to desired initial concentrations of 40, 80, 120, 180 and 220 mg/l.

Adsorbent preparation

Chitosan beads formation

75.3 g of chitosan flakes was dissolve in 1 l of 3.0% (v/v) acetic acid solution. The chitosan solution obtained was filtered through a polystyrene sieve with mush 100 μm to remove impurities. The filtered chitosan solution was pumped with a peristaltic pump through a glass pipette. Upon contact with 1 M sodium hydroxide solution, the anti-solvent induces the formation of chitosan gel beads. The wet chitosan beads was rinsed several times with distilled water and filtered to remove any residual sodium hydroxide.

Preparation of cross-linked chitosan beads

Chitosan cross-linked with glutaraldehyde was obtained by placing the prepared chitosan beads in 0.5% glutaraldehyde solution. The suspensions were shaken manually and allowed to equilibrate for 24 h with intermittent manual shaking. The cross-linked beads were rinsed intensively with distilled water to remove the excess glutaraldehyde.

Grafting of the cross-linked beads

The beads were grafted according to the procedure outlined by Igberase et al. [10]. Briefly, 0.45 g/l of cross-linked chitosan beads and 0.1 g/l of aniline were transferred into 200 ml of 0.4 m/l HCl in a round-bottom flask and content was continuously stirred by a magnetic stirrer. After 30 min, 0.35 g of ammonium persulfate was added to the reactive medium and this was taken as zero time. Grafting was allowed to take place for an hour at 35 °C. The grafted cross-linked beads were washed with N-methyl pyrrolidinone (NMP) to remove any free or inactive polyaniline. Finally the grafted polymer was rinsed with distilled water and ready to be used.

Characterization of the beads

Approximately 0.45 g chitosan beads, cross-linked chitosan beads and GXCS was separately weighed, oven dried overnight at 60 °C and grinded to its powdered form. The grinded beads were measured with a Shimadzu XRD, model 7000. SEM analysis was conducted by bisecting the various set of beads and coating them with gold. The coated beads was then measured with a Jeol 733, superprobe.

Adsorption experiment

The adsorption experiments were conducted at different solution pH, adsorbent dosage, contact time, initial concentration and temperature in 100 ml Erlenmeyer flasks.

The effect of solution pH on the adsorption of Cd(II) and Pb(II) onto GXCS was investigated by separately mixing 0.45 g of the adsorbent in 100 ml sample having an initial concentration of 40 mg/l. The pH of the samples was adjusted by 0.1 M HCl and 0.1 M NaOH to various pH values in the range of pH 2–8. The temperature and agitation speed were fixed at 25 °C and 120 rpm respectively, while the flasks were shaken for 150 min. The effect of adsorbent dosage on the adsorption of metal ions was conducted by separately mixing GXCS in the range of 1.5–6.0 mg/l in 100 ml sample having an initial concentration of 40 mg/l. The effect of contact time was studied over a time range of 30–180 min while the effect of initial concentration was investigated at a concentration range of 40–220 mg/l. Adsorption isotherms were conducted at temperatures of 25–45 °C. Kinetics of adsorption was performed