The adsorption of copper (II) ions by polyaniline graft chitosan beads from aqueous solution: Equilibrium, kinetic and desorption studies

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ABSTRACT

In this study, chitosan beads were produced from chitosan flakes and grafted with polyaniline to enhance the adsorption properties of chitosan based material for copper (II) ions. Chitosan and polyaniline graft chitosan beads (PGCB) were characterized by FTIR and SEM to provide evidence of successful grafting. The effect of pH, pH_{pzc}, contact time and initial concentration was investigated in a batch system. Equilibrium data were obtained from the adsorption experiment carried out at different initial ion concentration. The data were fitted to the Langmuir and Freundlich isotherm at temperatures of 25 °C, 35 °C and 45 °C. The Langmuir model gave the best fit for both adsorbent. The maximum adsorption capacity for chitosan and PGCB at a temperature of 45 °C was found to be 52.6 mg/g and 100 mg/g, respectively and at a solution pH of 5. Thermodynamic parameters of the adsorption process such as the standard Gibb's free energy change ($\Delta G°$), standard enthalpy change ($\Delta H°$), and standard entropy change ($\Delta S°$) were calculated, and the result showed that adsorption of copper onto PGCB is spontaneous and endodermic in nature. The pseudo-first-order and pseudo-second-order were used to analyze kinetic data. The data fit well with the second-order kinetic model. Desorption of copper ions from loaded PGCB was efficient, 0.5 M HCl was successfully used in desorbing the beads loaded with copper ions and a percentage desorption of 97.1% was achieved at contact time of 180 min.

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Introduction

In recent years, there have been an increase in industrial activities and this has led to a tremendous increase in the application of heavy metals [1]. The major sources of these metal ions are industries such as mining, metal-plating, pharmaceutical, electrical device manufacturing and pest-control [2]. This development has produced quite a number of physical and chemical pollutants that find their way into water bodies. Copper for example is used extensively in the electrical industry and manufacture of fungicides. Although copper can be an essential element for human beings in trace amount due to the fact that human body can regulate the trace level haemostatically, it can also be toxic when large dosage is ingested [2]. The maximum contaminant level for Cu(II) in industrial effluent as suggested by United States Environmental Protection Agency (USEPA) is 1.3 mg/l [3].

Copper ions can be removed from water or wastewater physically or chemically due to the fact that they are un-biodegradable. Several techniques have been proposed for the removal of copper ions from water and wastewater including

chemical precipitation, membrane filtration, ion exchange, electrolysis and adsorption [4,5]. Most of these methods are inefficient when it comes to treating water with low metal concentration [6]. For example, precipitation method is limited by; labor-intensive operation, cost and lack of selectivity of the precipitation process [6]. In the case of membrane filtration which is often guided by the membrane pore, it is inefficient in meeting the requirement of low metal concentration and the other disadvantage to be cost of the membrane which is very expensive. Recent studies have shown adsorption to be the most promising technique for metal ions removal due to convenience, easy operation, simplicity of design and can remove different type of pollutants [7].

The use of chitosan as an adsorptive polymer in removing a wide range of contaminant has been a major development in the past years [8]. Chitosan is a polymer derived from N-deacetylation of chitin [9], a naturally occurring polysaccharide obtained from crustaceans i.e. shrimps and crabs, and fungal biomass. This polymer is well established as an excellent natural adsorbent for metal ions removal due to the presences of the amino ($-NH_2$) and hydroxyl ($-OH$) groups. These groups serve as the coordination and binding sites [10]. However, the end product of chitosan is chitosan flakes during the production process, but this flake is not efficient in adsorption processes due to its poor adsorption characteristics which may result to low adsorption capacity. To overcome this problem of poor adsorption performance, flakes are converted into

chitosan gel beads [11]. This transformation is necessary for ease of handling and easier diffusion of target metal ions to adsorption site. Several grafting of chemicals with chitosan beads have been reported in literature to create additional adsorption site, thereby improving its adsorption performance in the process. Such chemicals include; polyacrylamide, acrylonitrile and carboxylic acid [12–14]. This report investigates the possible use of polyaniline grafted chitosan beads (PGCB) as an adsorbing material for copper ions. Since polyaniline has amine group that is capable of binding metal ions, it is therefore necessary to develop an adsorbent that will adsorb copper ions much better than other chitosan based materials. For this purpose chitosan flakes was converted to chitosan beads. The beads were grafted with polyanilne and then characterized using physical techniques such as Fourier transformed infrared (FTIR) and scanning electron microscope (SEM). The effect of adsorption parameters such as solution pH, pH_{pzc}, contact time and initial concentration was investigated. The Langmuir and Freundlich models were used to describe adsorption isotherms for chitosan and PGCB. The thermodynamics of adsorption of copper (II) onto PGCB was described by parameters such as standard Gibb's free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) while the pseudo first-order and pseudo second-order kinetic model was used to describe kinetic data for the PGCB. The effect of eluents (HCl and HNO_3) on percentage desorption of PGCB loaded copper (II) ion was also investigated. In determining the reusability of the PGCB loaded copper (II) ion, three cycles of adsorption/desorption studies was carried out.

Methods

Materials

The chitosan flakes with average molecular weight 400 kDa and a degree of deacetylation of 74% was obtained from Labchem. Chitosan flakes were used to prepare the beads. Aniline (99.5%, extra pure) was purchased from AEC AMERSHAM (PTY) LTD, and was used without any further purification. Ammonium persulfate (>98%), hydrochloric acid (99%), 1-methyl-2-pyrrolidinone (>99%), sodium hydroxide (>99%), acetic acid (>99%) and potassium nitrate were all purchased from Sigma–Aldrich. Distilled water was produced with a pure water distiller (Ultima 888 water distiller) in the school laboratory. The pH of the solution was measured with a pH meter (Hanna HI 8421), purchased from Sigma–Aldrich.

Preparation of the beads

A 70% (w/w) chitosan solution was made by dissolving 75.3 g of chitosan flakes in 1 L of 3.0% (v/v) acetic acid solution [15]. The dissolved chitosan solution was filtered through a polystyrene sieve with mush 100 μm to remove impurities, formation of chitosan gel beads is said to take place when the filtrate comes in contact with 1 M of sodium hydroxide solution.

Grafting of the beads

0.45 g/l of chitosan beads and 0.1 g/l of aniline were transferred into 200 ml of 0.4 g/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 PGCB was washed with N-methyl pyrrolidinone (NMP) to remove any free or inactive polyaniline. Finally the grafted polymer (Fig. 1) was rinsed with distilled water and ready to be used.
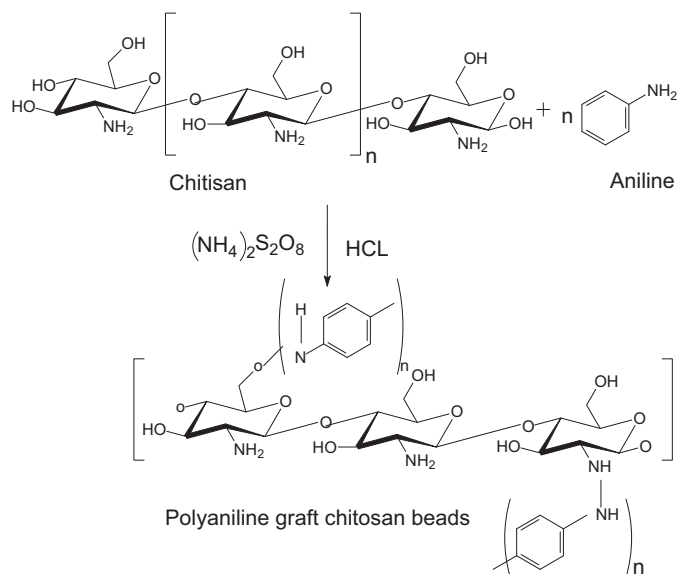

Fig. 1. Graft copolymerization of aniline onto chitosan.

Characterization of the grafted beads

Infrared measurement

Approximately 0.45 g of chitosan and PGCB was separately weighed and oven dried overnight at 60 °C and blended to its powdered form. The blended beads were measured with a shimadzu FTIR, model 8300 (Kyoto, Japan).

SEM measurement

Approximately 0.45 g of chitosan and PGCB was separately weighed and bisected in other to get a clear vision of the inner fibers. The bisected beads were coated with gold and measured with a Jeol 733, superprobe.

Adsorbate preparation

Stock solution of Cu(II) was prepared by dissolving required amount of $CuSO_4 \cdot 5H_2O$ in distilled water. The stock solution was further diluted to obtain various initial concentrations (40, 80, 120, 200, 320 and 400 mg/l).

Effect of pH

Samples of 100 ml having an initial concentration of 40 mg/l was transferred into a series of Erlenmeyer flasks, 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. Then, 0.45 g of chitosan and PGCB was separately added to each flask. The flasks were placed in a labcon incubator and shaken for 150 min. The temperature and agitation speed were fixed at 25 °C and 120 rpm respectively. After equilibrium, a clear metal solution was taken and analyzed with atomic adsorption spectrophotometer to determine the amount of metal ion adsorbed on the beads.

Determination of pH_{pzc}

The point of zero charge (pH_{pzc}) of chitosan and PGCB was determined by method outlined by Ofomaja and Ho [16]. To a series of 100 ml Erlenmeyer flasks, 45 ml of KNO_3 solution of known concentration was transferred. The pH_i values of the solution were adjusted from pH 2 to 8 by adding ether 0.1 M HCl or NAOH. The total volume of the solution in each flask was made up