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Research paper

Utility of chemically modified agricultural waste okra biomass for removal of toxic heavy metal ions from aqueous solution

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A R T I C L E I N F O

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A B S T R A C T

Agricultural waste biomass has recently gained attention in the field of wastewater remediation because of their abundance and renewable nature. In the present study, agricultural waste cellulosic biomass has been modified through succinylation reaction and subsequently used as an adsorbent for the removal of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} toxic metal ions from aqueous solution. The removal of metal ions from aqueous solution was investigated as a function of pH, contact time, temperature and metal ion concentration. Pseudo-second-order kinetic model was used to study adsorption kinetics for all metal ions. Langmuir isotherm model was applied to describe the adsorption isotherm and maximum adsorption capacity q_m calculated for Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} metal ions were 72.72, 57.11, 121.51 and 273.97 mg/g respectively. The thermodynamic parameters ΔH° and ΔG° values for metals ion adsorption on the succinylated okra biomass adsorbent showed the process to be spontaneous and exothermic in nature.

1. Introduction

Water is the most essential and important component on the earth for the sustenance of life. Contamination of water with heavy metal ions such as cadmium, lead, copper, chromium, arsenic, nickel and zinc is an ongoing problem due to their toxicity towards living species. Heavy metal-contaminated wastewater can originate from various industries such as printing, dyeing, metallurgical engineering, electroplating, photographical materials, fuels, power operations, semiconductors and battery manufacturing (Kadirvelu et al., 2001; Williams et al., 1998; Wang and Chen, 2009). Unlike organic wastes, these heavy metal ions are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders; therefore they must be removed before discharge (Wan Ngah and Hananfiah, 2008). These metals are toxic even at very low concentration. Thus levels of heavy metals in water, waste water and agriculture water must be reduced to a maximum permissible concentration.

Traditional methods such as chemical precipitation, coagulation, solvent extraction, ion exchange, electrolysis, reverse osmosis, membrane separation and adsorption on activated carbon have been used for the removal of heavy metals from industrial waste water streams (Xiangliang et al., 2005; Gurgel et al., 2008). Most of these methods are extremely expensive (Ng et al., 2002) and cannot used on large scale applications. Adsorption is now recognized as a promising, efficient and economic technique for removal of metal ions from aqueous solution (Crini, 2005). Activated carbon has been most widely used adsorbent; however it possesses lot of disadvantages such as high operating cost, low selectivity and complex thermal regeneration requirements. Recently low cost adsorbents from agricultural waste biomass and cellulosic biomasses have attracted the attention of scientists due to its ability to remove toxic metal ions more effectively in comparison to other method mentioned above (Wan Ngah and Hananfiah, 2008; Abdel-Halim and Al-Deyab, 2011). The biomass derived from agriculture wastes has received particular attention as an attractive alternative as adsorbents because of their chemical stability and high reactivity resulting from the presence of repetitive functional groups in cellulosic chain.

Adsorption on agricultural waste cellulosic biomass has been an attractive approach due to their non-toxic nature, low cost, high efficiency, formation of low sludge and regeneration of adsorbent (Dhiraj et al., 2008). These fibers have abundant and specific functional group such as hydroxyl groups which have affinities for heavy metal ions. In cellulose hydroxyl groups are involved in intermolecular hydrogen bonds thus leading to low adsorption capacities (Wan Ngah and Hananfiah, 2008). Chemical modification

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of cellulosic biomass by chemical treatment is carried out to achieve efficient adsorption capacity for heavy metal ions. Chemical modification provides more active binding sites are provided, better ion-exchange properties are obtained and new functional groups are formed through chemical modification (Wan Ngah and Hananfiah, 2008; Xiangliang et al., 2005; Gurgel et al., 2008; Ng et al., 2002; O'Connell et al., 2008; Kamel et al., 2012). Various methods are based on using chemical agent which contains amine, amidoxime, carboxylate and hydrazide functional groups (Jiang et al., 2009; Singha and Guleria, 2014; Monier et al., 2010). Succinylation reaction has also been found to be a good tool for modification of fibers (Hokkanen et al., 2013; Gellerstedt et al., 2002). Various cellulosic biomass including rice husks, spent grain, sawdust, sugarcane bagasse, fruit wastes, weeds and banana stem fibers have been used as adsorbents in wastewater treatment applications (Wan Ngah and Hananfiah, 2008; Anirudhan et al., 2010). Among these natural biomasses, cellulosic okra fiber is another potential biomass which can be used as adsorbent for wastewater treatment. Okra fiber is an agricultural waste biomass principally composed of cellulose, hemicellulose and lignin. Okra fibers are extracted from the stem of a plant of the Malvaceae family which is originally from Egypt, but plant is cultivated in tropical, subtropical and warm temperate regions around the world for nutritional purposes.

In the present study, we reported the preparation of succinylated cellulosic biomass by using succinic anhydride as a modifying agent. Further succinylated cellulosic fibers have been used for removal of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} heavy metal ions from aqueous solution. The adsorption parameter including effects of time, metal ion concentration and temperature on adsorption were investigated. Regeneration studies, using nitric acid at different concentrations, were also carried out.

2. Material and methods

2.1. Materials

Okra cellulosic biomass was extracted and made free from impurities by the method earlier reported in the literature (Singha et al., 2013). The dried fibers was then grinded with a strong grinder and further ball milled for one hour till the particle size was reduced to 6°μm. Then, it was dried at 90 °C in an oven and stored in desiccator. Succinic anhydride (SA) and pyridine supplied by E-Merck, chemicals limited, Mumbai (India) was used as received. The chemicals and solvents such as sodium hydroxide, acetic acid, methylene chloride, acetone, nitric acid and dimethylformamide were of analytical grade and used without further purification. All other chemicals were analytical grade or above and used as received without further purifications.

2.2. Chemical modification of cellulosic biomass

2.2.1. Cellulosic biomass mercerization

Cellulosic biomass (10 g) was treated with aqueous 2 mol/L NaOH solution at 25 °C for 3 h under constant stirring in order to obtain mercerized okra biomass. At the end of each treatment, the alkali was separated from okra biomass by filtration through sintered filter, washed with distilled water up to pH 7 and acetone. The mercerized cellulosic fibers were then dried at 70 °C in an oven for 1 h and stored in desiccator. The percent mass loss (mpl) was calculated at the end of treatment.

$$\text{Percent mass loss (mpl)} = \frac{M_1 - M_2}{M_1} \times 100 \quad (1)$$

where M_1 the mass of okra biomass before treatment and M_2 is the mass of cellulosic biomass after alkali treatment.

2.2.2. Succinylation of mercerized cellulosic biomass

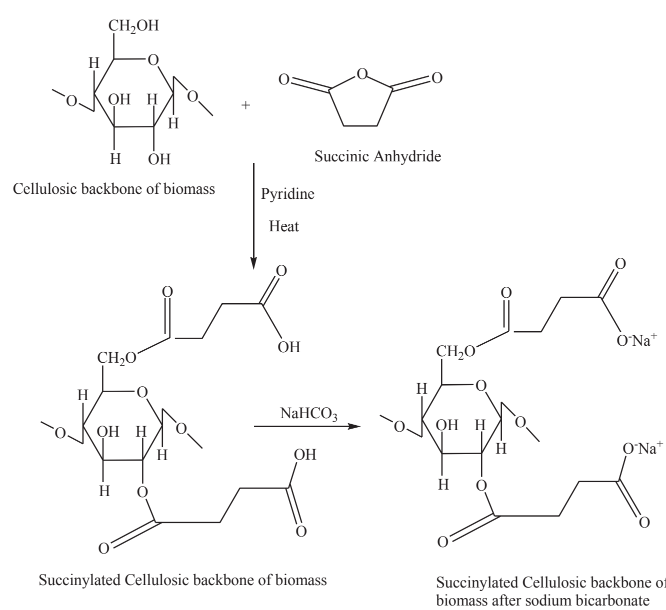
Mercerized cellulosic biomass (10 g) was carried by refluxing with succinic anhydride (20 g) in pyridine (300 mL) for 16 h. The chemically modified material was separated by filtration through sintered filter, washed in sequence with: solution of acetic acid in dichloromethane (1 mol/L), ethanol 95%, distilled water, hydrochloric acid solution (0.01 mol/L), distilled water and finally with acetone. In order to liberate carboxylate functions for a better chelating function than the carboxylic group, succinylated cellulosic biomass was treated with a saturated sodium bicarbonate solution for 60 min under constant stirring and afterwards filtered and finally washed with distilled water and then acetone. After drying at 70 °C in an oven for 1 h and modified biomass was kept in desiccator overnight and mass percent gain (mpg) was calculated.

$$\text{Percent mass gain (mpg)} = \frac{M_3 - M_2}{M_2} \times 100 \quad (2)$$

where M_2 the mass of alkali cellulosic biomass before succinylation treatment and M_3 is the mass of cellulosic biomass after succinylation treatment.

2.2.3. Degree of functional groups introduced by succinylation

The succinylation reaction led to introduction of carboxylic groups in the cellulosic biomass as also shown in Scheme 1. The concentration of carboxylic groups introduced in the biomass was determined by the method as reported in the literature (Gurgel et al., 2008; Liu et al., 2010). For this, 0.05 g of succinylated biomass was treated with 100.0 mL of an aqueous NaOH solution (10 mmol/L) in a 250-mL Erlenmeyer flask for 1 h under constant stirring. Soon thereafter, the treated biomass was separated by single filtration and three aliquots (25.0 mL) of each obtained solution were titrated with an aqueous HCl solution (10 mmol/L) using phenolphthalein as an indicator. The above solution was back-titrated until the solution turned from the pale pink to



Scheme 1. Reaction scheme for the modification of cellulosic biomass with succinic anhydride.