Lead removal onto cross-linked low molecular weight chitosan pyruvic acid derivatives

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A B S T R A C T

Adsorption capacity of cross-linked low molecular weight chitosan pyruvic acid derivatives $CS_nPA\text{-}GLA$ ($n = 8, 11$) were examined by employing 2^3 factorial design method. Three (3) factors and two (2) levels of adsorbent dose (A) (0.05 and 0.1 g), adsorbent type (B) ($CS_8PA\text{-}GLA$ and $CS_{11}PA\text{-}GLA$) and concentration of lead solution (C) (1 and 3 mg/L) were considered. From the statistical analysis, all the main parameters (A, B and C) and some interactions of the main parameters (AC and ABC) had influence on the adsorption process at 5% significance level. The adsorption process was greatly influenced by the adsorbent type (B). The adsorption equilibrium results correlated well with the Freundlich isotherm model. The adsorption kinetic data also correlated well with the pseudo second order. The thermodynamic studies also revealed that the nature of lead adsorption was spontaneous and endothermic. The findings suggest that $CS_8PA\text{-}$ GLA is better than $CS_{11}PA\text{-}GLA$ for lead sorption.

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1. Introduction

Removal of lead from the environment has received needed awareness due to their toxicity, carcinogenicity and other adverse effects (Wu et al., 2013). Wastewater from industries such as metallurgical alloying, glass, battery, mining, printing, ammunition, ceramics, among others (Eren, 2009; Li et al., 2012) are the major sources of lead contamination. Precipitation, complexation, reverse osmosis, ion-exchange, adsorption, among others are techniques employed for heavy metal elimination. Among the aforementioned techniques, adsorption has been identified as a striking process because of its effectiveness and easiness in use for the elimination of metal ions (Sreńscek-Nazzal, Kamińska, Michalkiewicz, & Koren, 2013). Commercial activated carbon is microporous in nature and has excellent adsorption capacity and surface area. This makes it a good material for the elimination of metal ions, however, the high operational cost cannot be overlooked. Consequently, inexpensive adsorbents are attracting the spotlight of numerous experiments for the elimination of metal ions. Among these inexpensive

adsorbents, the most admired for the elimination of metal ions is chitosan (Kavianinia, Plieger, Kandile, & Harding, 2012; Rajic et al., 2010). Structurally, chitosan has hydroxyl and amino groups which is good for metal ions sorption. Again, the source and experimental condition of the preparation of chitosan determines its adsorption capacity (Orrego et al., 2010). The adsorption properties of chitosan could be improved via physical or chemical process, and the chemical process includes cross-linking, carboxymethylation, hydroxylation, sulfonation, quaternarization among others. In the midst of the derivatives, modification of chitosan with carboxylic groups has been considered often as a fascinating process for escalating the adsorption capacity of chitosan (Ma, Wang, Zhao, & Tian, 2012). Many researchers have modified chitosan with carboxylic groups to obtain carboxymethyl chitosan (CMC), but modification of different low molecular weight chitosans with pyruvic acid (PA) has not been done so far. CMC has multi-functional groups such as $-OH$, $-NH_2$, $-COOH$ and makes it exhibit higher affinity for metal ions (Wang, Qin, Ding, Peng, & Wang, 2010). On the other hand, CMC is soluble in pH ≤ 7, so it is necessary to cross-link it with glutaraldehyde to make it insoluble in acidic solution and water.

In this study, chitosan was degraded into two kinds of low molecular weight chitosan (CS_8 and CS_{11}), modified with pyruvic acid (PA) and then cross-linked with glutaraldehyde (GLA) to obtain $CS_8PA\text{-}GLA$ and $CS_{11}PA\text{-}GLA$. In order to evaluate the importance of adsorbent dosage, adsorbent type and Pb (II) concentration, 2^3 full

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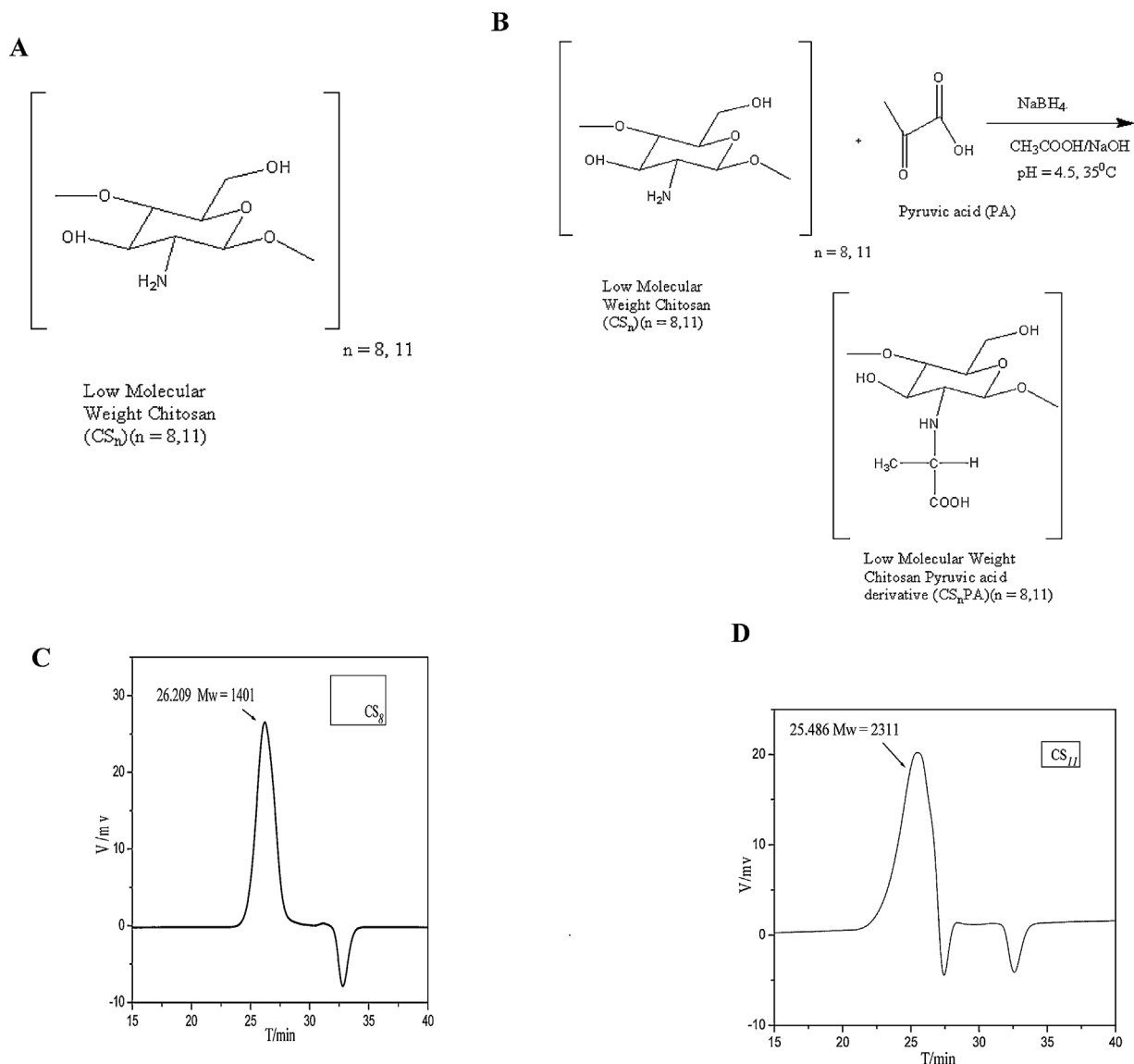
Fig. 1. Structure of low molecular weight chitosan (CS_n) ($n = 8, 11$) (A); modification of low molecular weight chitosan (CS_n) ($n = 8, 11$) with pyruvic acid (PA) (B); size exclusion chromatography (SEC) of CS_8 (C); size exclusion chromatography (SEC) of CS_{11} (D).

factorial design was used. Factorial design was used to cut down the overall research cost, the number of experiments and time. Also, it was used to determine which main factors or combined factors effects were statistical significant for the elimination of lead ions and how a factor varied according to the level of the other factors.

2. Materials and methods

2.1. Materials

Chitosan (CS) (molecular weight = 200 kDa Degree of deacetylation = 95%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), hydrogen peroxide, pyruvic acid (PA), glutaraldehyde (GLA) and all other chemicals and reagents were of analytical grade. Distilled water was used to prepare solutions.

2.2. Preparation of low molecular weight chitosan (CS_n) ($n = 8, 11$) using microwave

The method from our laboratory was employed in the preparation of low molecular weight chitosan (Zhang, 2009). 2 g of chitosan

(CS) was weighed and placed in a three mouth flask (250 mL). 160 mL of 0.5% aqueous acetic acid was added and mechanically stirred for 10 min. 4 mL of H_2O_2 (30%) was dropped slowly, and the mixture was agitated mechanically for 2–3 min. Degradation at 90 °C, 600 W for 30 and 50 min were done to obtain CS_{11} and CS_8 respectively using microwave. The solution pH was attuned to neutral using KOH solution (2 M) at 25 °C, and insoluble impurities were removed by vacuum filtration. The solution was evaporated to a proper amount in a single flask (250 mL) with a rotary evaporator and precipitated with anhydrous ethanol. A vacuum oven was used to dry the low molecular weight chitosan (CS_n) ($n = 8, 11$) at 30 °C after filtration and washed with anhydrous ethanol. The structure of low molecular weight chitosan (CS_n) ($n = 8, 11$) is shown in Fig. 1A.

2.3. Modification of low molecular weight chitosan (CS_n) ($n = 8, 11$) with pyruvic acid (PA)

20 mL of 0.20 M acetic acid was added to 1 g of CS_n ($n = 8, 11$). Ten drops of acetic acid (99.5%) and 70 mL of methanol were added afterwards. Pyruvic acid (2.825 g) dissolved in 10 mL of methanol