Food Chemistry 181 (2015) 133–139

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Modification of porous starch for the adsorption of heavy metal ions from aqueous solution

Xiaofei Ma [a], Xueyuan Liu [a], Debbie P. Anderson [b], Peter R. Chang [b,c,*]

[a] School of Science, Tianjin University, Tianjin 300072, China
[b] Bioproducts and Bioprocesses National Science Program, Agriculture and Agri-Food Canada, 107 Science Place, Saskatoon, SK S7N 0X2, Canada
[c] Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, SK S7N 5A9, Canada

ARTICLE INFO

Article history:
Received 20 October 2014
Received in revised form 16 February 2015
Accepted 17 February 2015
Available online 24 February 2015

Keywords:
Porous starch
Adsorption
Starch xanthate
Starch citrate
Starch modification
Heavy metal ions

ABSTRACT

Porous starch xanthate (PSX) and porous starch citrate (PSC) were prepared in anticipation of the attached xanthate and carboxylate groups respectively forming chelation and electrostatic interactions with heavy metal ions in the subsequent adsorption process. The lead(II) ion was selected as the model metal and its adsorption by PSX and PSC was characterized. The adsorption capacity was highly dependent on the carbon disulfide/starch and citric acid/starch mole ratios used during preparation. The adsorption behaviors of lead(II) ion on PSXs and PSCs fit both the pseudo-second-order kinetic model and the Langmuir isotherm model. The maximum adsorption capacity from the Langmuir isotherm equation reached 109.1 and 57.6 mg/g for PSX and PSC when preparation conditions were optimized, and the adsorption times were just 20 and 60 min, respectively. PSX and PSC may be used as effective adsorbents for removal of heavy metals from contaminated liquid.

1. Introduction

When heavy metals from various industrial activities enter aquatic systems, they must be removed from the wastewater because of their significant threat to human health. Among the various techniques used for treatment of heavy metals in wastewater, adsorption is a promising alternative due to ease of handling, low operating costs, high efficiency for removing very low levels of heavy metals from dilute solutions, and there is no threat of secondary contamination.

There are many adsorbents that can be used to remove heavy metals from aqueous solutions including oxidized carbon nanotubes (Tofighy & Mohammadi, 2011), graphene oxide (Wang, Yuan, et al., 2013), clay (Sdiri, Higashi, Chaabouni, & Jamoussi, 2012), and biomass sources (Altun & Pehlivan, 2012; Jain, Garg, & Kadirvelu, 2009; Kaya, Pehlivan, Schmidt, & Bahadie, 2014; Wang, Yin, et al., 2013). Natural polysaccharide-based adsorbents have been focused on because of their low cost, availability, and biodegradability. The building blocks of biomass-based polysaccharides have a substantial number of reactive hydroxyl, carboxyl, and/or amino groups that can be further modified for the removal of heavy metals. For example, a magnetic chitosan adsorbent was synthesized by surface modification of chitosan/SiO_2/Fe_3O_4 with EDTA using 3-ethyl-1-(3-dimethylaminopropyl) carbodiimide hydrochloride as the crosslinker in a buffer solution (Ren, Abbood, He, Peng, & Huang, 2013). This adsorbent could be collected using a magnetic separation process after Cu^{2+}, Cd^{2+} and Pb^{2+} were removed from the solution. In another study, a hybrid gel fabricated by crosslinking calcium alginate and gamma-poly glutamic acid was used to adsorb Nd^{3+} (Wang et al., 2014). In addition, carboxylic acid functionalized deacetylated konjac glucomannan was used to remove heavy metals from water (Liu, Luo, Lin, Liang, & Chen, 2009). Meanwhile, cellulose xanthogenates derived from straw were prepared for use as adsorbents of heavy metals by sulfonation and magnesium substitution (Deng et al., 2012). Additionally, crosslinked amino starch was obtained by reacting ethylenediamine with dialdehyde starch for the adsorption of Cu^{2+} and Cr^{6+} (Dong et al., 2010).

Among biomass-based polysaccharides, starch and cellulose are the most promising raw materials with low cost and universality. During conventional modification of starch or cellulose, strong acid or base at high concentration is commonly used to destroy the intermolecular hydrogen bond interactions and crystallization regions, which then facilitates the chemical reaction between the starch and modifiers. Conversely, we postulate that porous starch (PS) with a large specific surface area and low crystallinity could foster effective modification under moderate reactive conditions

---

[*] Corresponding author at: Bioproducts and Bioprocesses National Science Program, Agriculture and Agri-Food Canada, 107 Science Place, Saskatoon, SK S7N 0X2, Canada. Tel.: +1 306 385 9449; fax: +1 306 385 9482.

E-mail address: peter.chang@agr.gc.ca (P.R. Chang).

http://dx.doi.org/10.1016/j.foodchem.2015.02.089
0308-8146/

while maintaining the porous structure. We believe that the porous starch xanthate (PSX) and porous starch citrate (PSC) prepared here have not been reported in the literature.

It is interesting to note that adsorbents prepared from the modification of polysaccharides are usually soluble or in a powder form, and so are difficult to separate out after the adsorption process. Contrary to the prior art, we postulate using PS for easy and economical solid–liquid separation. Such an attempt has not been explored previously. In this work, PS was prepared by replacing ice crystals in the frozen starch gel with ethanol using a solvent exchange technique (Qian, Chang, & Ma, 2011) and later modified with carbon disulfide (CD) and citric acid (CA) at low concentrations of NaOH or without NaOH. Subsequently, the adsorption patterns of Pb^{2+} ions by PSX and PSC were characterized.

2. Materials and methods

2.1. Materials

Potato starch was purchased from Manitoba Starch Products (Manitoba, Canada). Ethanol, carbon disulfide, citric acid and other chemicals were all analytical grade.

2.2. Preparation of porous starch (PS)

The preparation of PS was based on the method of Chang, Yu, and Ma (2011). Potato starch (5 g) was added to 100 mL of distilled water and heated at 90 °C for 0.5 h to completely gelatinize the starch. The mixture was refrigerated for a few days at 5 °C until a

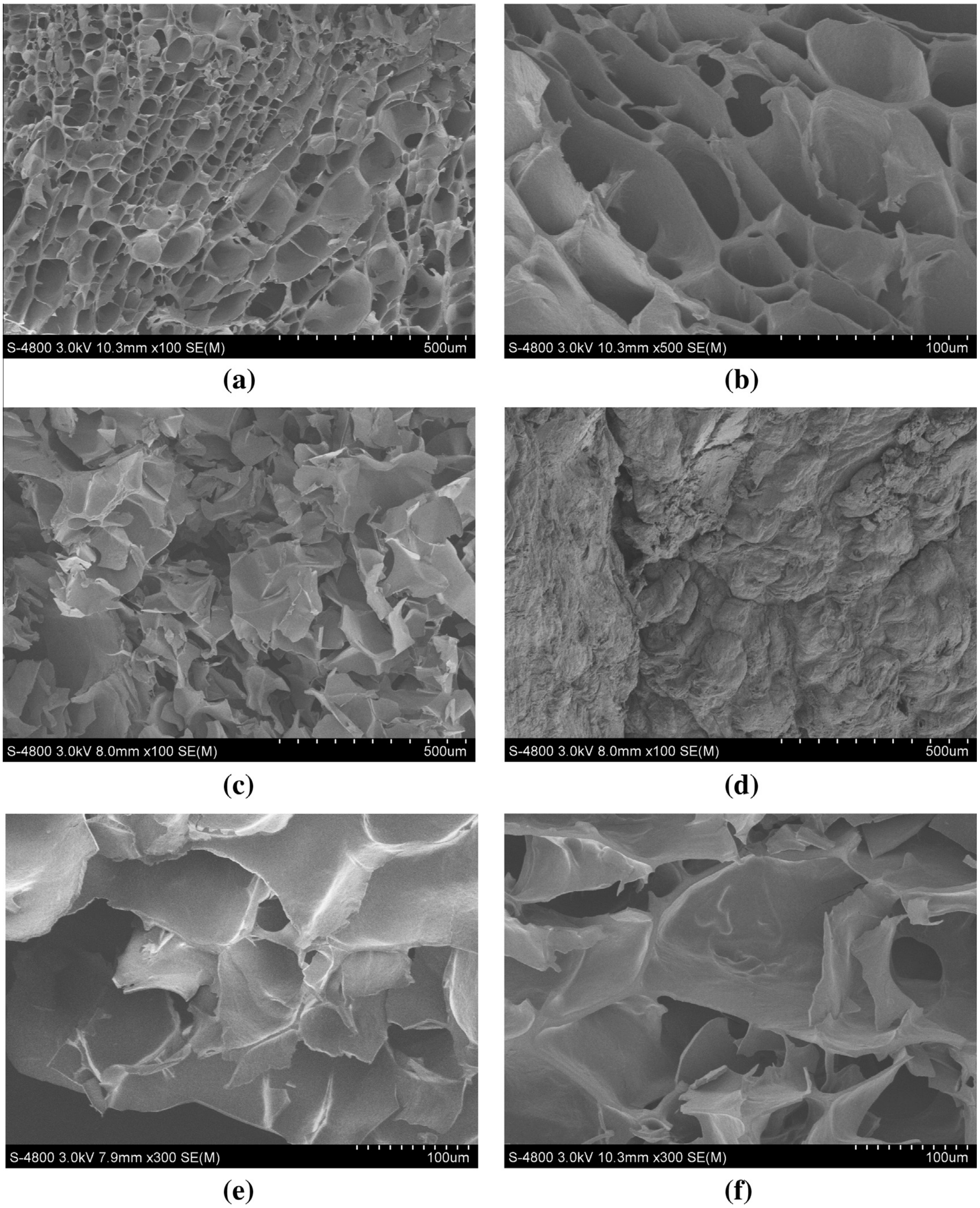

Fig. 1. SEM images of PSX1.35 prepared from 0.5% NaOH (a and b); PSX0.54 prepared from 5% NaOH (c); PSX1.35 prepared from 5% NaOH (d); PSC0.1 (e); and PSC1.0. (f).