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# Succinate-bonded pullulan: An efficient and reusable super-sorbent for cadmium-uptake from spiked high-hardness groundwater

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## ARTICLE INFO

### Article history:

Received 2 February 2015

Revised 7 April 2015

Accepted 9 April 2015

Available online 4 July 2015

### Keywords:

Adsorption

Cadmium

Modified pullulan

Succinylation

Thermal stability

## ABSTRACT

Chemically modified pullulan was evaluated for its sorption efficiency and selectivity to remove cadmium (Cd) from spiked high-hardness groundwater (GW). Pullulan esterified with succinic anhydride using dimethylaminopyridine showed a fairly high degree of substitution value as confirmed by <sup>1</sup>H NMR spectroscopy. Pullulan succinate (Pull-Suc) was converted into the sodium salt (Pull-Suc-Na). The effect of contact time (5–200 min) and pH (2–8) on Cd-uptake by the sorbent (Pull-Suc-Na) was investigated. The sorbent showed more than 90% Cd-removal in first 15 min from distilled water (DW) and GW solution, respectively. Comparison of Pull-Suc-Na with other polysaccharidal sorbents suggested its high efficiency (DW 476.2 mg/g and GW 454.5 mg/g) and selectivity for the removal of Cd by an ion exchange mechanism, which is further supported by the negative Gibbs free energy values calculated from Langmuir isotherms. A Langmuir isotherm kinetic model provided the best fit for the sorption of Cd using Pull-Suc-Na. The sorbent showed a negligible decrease in Cd-uptake over three regeneration cycles. The thermal stability testing of the sorbents indicated that Pull-Suc-Na (sorbent) is more stable than Pull-Suc.

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## Introduction

Cadmium (Cd) is a highly toxic environmental pollutant present in ground water (GW) as a result of waste disposal from industries such as mining, metallurgy, metal finishing, electronics, smelting, alloy manufacturing, plastics, fertilizers, pesticides, textile operations, pigments and nickel–cadmium (Ni–Cd) batteries (Nguyen et al., 2013; Yan et al., 2015; Duan et al., 2014; Liu et al., 2013). The non-biodegradability of Cd may result in its accumulation within living tissues through the food chain (Zhang et al., 2013a). Decrease in activity of metallo-enzymes due to replacement of Zn ion by Cd ion,

kidney dysfunction, multiple bone fractures, cancer at multiple sites, lung cancer (Khan et al., 2013; Davis et al., 2006), prostate carcinogenesis (Zeng et al., 2004), elevation in blood pressure levels (Tellez-Plaza et al., 2008) and weight loss (Sud et al., 2008) are some major problems caused by increased levels of Cd in the human body.

Effective techniques for the removal of heavy metal ions from contaminated GW (Wang and Ren, 2014) include ion exchange (Wang and Fthenakis, 2005), adsorption by activated charcoal (Nadeem et al., 2009), binding and chelating with some natural (Zhang et al., 2013b; Tonietto et al., 2014; Wang and Chen, 2014; Shi et al., 2013) or synthetic polymers (Wei et

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al., 2015; Masoumi and Ghaemy, 2014), precipitation (Lin et al., 2005) and solvent extraction (Jia et al., 2004).

Being renewable and abundant, some low-cost sorbents mainly consisting of cellulosic materials such as agricultural waste (Won et al., 2014; Garg et al., 2008), fruit peels and plant barks (Prapagdee et al., 2014), carboxylated cellulose nanocrystals (Yu et al., 2013), have metal binding capacity and find application in removal of heavy metal ions. However, agricultural waste materials contain different types of functionalities; so that it cannot be established which type of functionality is responsible for metal uptake. Moreover, the sorption capacity of agriculture waste is also not appreciable. Therefore, there is an utmost need to introduce more efficient and selective sorbents with a single kind of functional group to obtain a defined and higher sorption capacity.

Naturally-occurring renewable biopolymers, e.g., cellulose, pullulan and dextran, have hydroxyl groups that can be modified by esterification (Hussain, 2010) with carboxylic acid anhydrides (Hussain et al., 2010a, 2010b). The resulting carboxylate groups grafted onto polysaccharides reportedly have a tendency to exchange cations from aqueous solution (De Melo et al., 2009). Therefore, by converting the cellulosic/polysaccharidal materials into sodium salts, particularly the succinate derivatives, the tendency for the selective removal of Cd increases many-fold, even in the presence of divalent cations generally present in water (De Melo et al., 2009; Belhafaoui et al., 2009).

Our objective was to synthesize a novel super-sorbent of a commercially available polysaccharide, i.e., pullulan, after its modification. An aim was to evaluate and compare modified pullulan sorbents in terms of their Cd-removal capacity from distilled water (DW) and GW. The present investigation also evaluated the reproducibility of the performance of regenerated sorbent. Besides sorption studies, comparative thermal studies of acidic and sodic forms of the sorbent were carried out.

## 1. Materials and methods

### 1.1. Materials

Pullulan (molecular weight 100,000) used in the current study was provided by Fluka and dried under vacuum at 110°C for 2 hr prior to use. GW was collected from the city outskirts of Sargodha (a city having water with high hardness and high ionic strength), Pakistan. The chemical characteristics of the GW (pH 7.2; total hardness 1510 mg/L (as CaCO<sub>3</sub>); Mg<sup>2+</sup> hardness 1163.5 mg/L; Ca<sup>2+</sup> hardness 346.5 mg/L; Cl<sup>-</sup> 1544 mg/L) were determined using known analytical techniques. All reagents and solvents used were of analytical grade.

### 1.2. Sample analysis

Fourier transform infrared spectroscopy (FT-IR, KBr, 4000–400 cm<sup>-1</sup>) spectra were measured on an IR Prestige-21 instrument (Shimadzu, Japan). Proton nuclear magnetic resonance (<sup>1</sup>H NMR spectra δ, ppm) of the products were acquired on a Bruker 400 MHz machine in deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>) at 40°C.

Thermogravimetric (TG) and derivative TG (DTG) analyses were recorded on thermal analyzer (SDT Q 600, TA Instruments, USA) for pullulan succinate (Pull-Suc) and sodium salt (Pull-Suc-Na). Thermal analyses were recorded at the onset of significant weight loss from heated samples. Samples were measured under nitrogen with a temperature increase of 10°C/min from ambient to 1000°C.

### 1.3. Synthesis of Pull-Suc conjugate and Pull-Suc-Na

An optically clear solution of pullulan (10.0 g, 61.6 mmol) was prepared in dimethylacetamide (DMAc, 30 mL) at 80°C under stirring for 1.0 hr. Succinic anhydride (37.0 g, 370 mmol) was added, followed by the addition of dimethylaminopyridine (DMAP, 500 mg) as a catalyst, and the reaction mixture was kept under stirring at 80°C for 24 hr. The product (Pull-Suc) was precipitated in ethanol (500 mL) and washed with ethanol (250 mL) three times to remove the unreacted reagents. The colorless precipitates were dried under vacuum at 50°C overnight.

Yield: 22.8 g (82%), degree of substitution (DS) = 2.84/Anhydroglucose repeating unit as calculated by <sup>1</sup>H NMR spectroscopy by comparing the signal intensities. FT-IR (KBr): 3395 (O–H), 2910 (C–H), 1719 (C=O<sub>Ester</sub>), 1026 (C–O–C) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ ppm): 2.37 (H-7), 2.77 (H-8), 3.14–4.75 (pullulan repeating unit-Hs).

The Pull-Suc-Na was prepared by alkaline treatment of Pull-Suc with saturated NaHCO<sub>3</sub> solution. The suspension was stirred at room temperature for 2.0 hr and then filtered. The solid was repeatedly washed with distilled water until neutral pH.

FT-IR (KBr): 3427 (O–H), 2912 (C–H), 1728 (C=O<sub>Ester</sub>), 1560 (COO<sup>-</sup>), 1022 (C–O–C) cm<sup>-1</sup>.

### 1.4. Calculation of DS

DS was calculated by stirring Pull-Suc (100 mg) in 0.02 mol/L NaHCO<sub>3</sub> solution (100 mL) for 2 h at room temperature. After filtration, a known volume of the NaHCO<sub>3</sub> solution was titrated against 0.02 mol/L HCl using methyl orange as an indicator. From the volume of HCl used, the DS of free carboxylic acid moieties was calculated using the following relations (Eqs. (1) and (2));

$$n_{\text{suc}} = V_{\text{NaHCO}_3} \times M_{\text{NaHCO}_3} - V_{\text{HCl}} \times M_{\text{HCl}} \quad (1)$$

where,  $n_{\text{suc}}$  is the number of moles of free carboxylic acid moieties;  $V_{\text{NaHCO}_3}$  is the volume of NaHCO<sub>3</sub> titrated against  $V_{\text{HCl}}$ ;  $M_{\text{NaHCO}_3}$  is the molarity of NaHCO<sub>3</sub>;  $M_{\text{HCl}}$  is the molarity of HCl.

$$\text{DS} = \frac{162.14 \times n_{\text{suc}}}{m_{\text{pull-suc}} - 100 \times n_{\text{suc}}} \quad (2)$$

where, 162.14 (g/mol) is the molar mass of an anhydroglucose unit; 100 g/mol is the net increase in the mass of an anhydroglucose unit for each substituted succinyl moiety;  $n_{\text{suc}}$  is number of moles of free carboxylic acid moieties;  $m_{\text{pull-suc}}$  is the mass in g of Pull-Suc analyzed.

The DS of the Pull-Suc was also calculated using <sup>1</sup>H NMR spectral analysis as described in references (Goodlett et al., 1971; Hussain et al., 2015).

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