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# Study on the preparation of orange peel cellulose adsorbents and biosorption of $Cd^{2+}$ from aqueous solution

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## Abstract

In this paper, orange peel modified with different chemical reagents as biosorbents were used to remove cadmium ion from aqueous solution. Effects of different chemical modifications on the biosorbent properties including washing, alkali saponification, cross-linking temperature and concentration of cross-linking reagent were investigated. Meanwhile, influence of pH of solution, initial cadmium concentration, shaking time and solid/liquid ratio on the removed of Cd(II) by different chemically modified biosorbents were studied. It can be concluded that cadmium ion could be removed by $0.6SCA_{80}$ (orange peel modified with 0.6 mol $L^{-1}$ citric acid under 80 °C after alkali saponification) biosorbent effective and quick. We obtained a series of biosorbents with the order of cadmium: $0.6SCA_{80} > SOP > CA2 > CA1 > PA1 > PA2 > OP$. For $0.6SCA_{80}$, the maximum capacity of cadmium was 0.90 mol $kg^{-1}$, the optimum pH value was 6, the reaction balance was established after shaking 120 min and the optimum solid/liquid ratio was 4.3 g $L^{-1}$. The desorption rate of cadmium was 94% with 0.15 mol $L^{-1}$ HCl solution. A comparison of different isotherm models revealed that the Langmuir isotherm model is fitted the experimental data best. The biosorption follows the Lagergren first-order kinetics model.

*Keywords:* Preparation; Orange peel; Cadmium; Biosorption

## 1. Introduction

Industrialization moves so rapid that the disposal of heavy metals into the environment increases accordingly. For example, cadmium is toxic priority pollutant, and wastewater that contains cadmium is harmful in the irrigational industrial applications. Cadmium is introduced into water from metal mines mining, melting, plating, cadmium nickel batteries, pesticide, oil paint, pigments, and alloy and sewage sludge. Tradition treatment methods include chemical precipitation, ion exchange, membrane processes and adsorption onto activated carbon and so on. It has been reported that the application of these methods is limited since they normally entail high operational costs or have removal efficiencies, which are insufficient for meeting the environmental requirements [1,2].

In the past few years, biosorption, bioprecipitation and uptake by biopolymers derived from agricultural wastes or microbes emerges as techniques that could provide alternative and/or additive processes for conventional physical and chemical methods for removing toxic ions from wastewater [3,4]. Such as coconut coirpith [5], pine bark [6], bagasse [7], barley [8], rice milling [9] papaya wood [10], bacterially [11], moss [12], seaweeds [13,14], corncob [15] and crab shells [16] have also been used for Cd(II) removal. Marshall et al. [17,18] have used agricultural by-products as adsorbents for removal of metal ions from aqueous solution.

Agriculture, forestry and fisheries have been generating large quantities of various biomass wastes and some of them contain various natural materials with interesting functional groups, such as carboxyl, hydroxy, amidocyanogen and so on. Orange peel is one of the valuable biomass wastes. Of the world total citrus fruits production, orange makes up 75%, and China is one of the major producers. The resultant large quantity of orange peel accounts for the feasibility of choosing it as raw material in this paper. Orange peel principally

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consists of cellulose, hemi-cellulose, pectin substances, chlorophyll pigments and other low molecular weight compounds like limonene and so on [19]. It has been reported that adsorption of metal ions such as Ni(II), Pb(II), Zn(II), Cu(II) and Co(II) were studied by using raw orange peel or orange peel modified with nitric acid [20,21], but the cadmium adsorption using orange peel modified with citric acid has not been reported. As the active binding sites for metals are supposed to be functional groups of hydroxyl and carboxyl in cellulose, we studied the adsorption behaviour of cadmium by chemically modified orange peel as adsorbents. Effects of different chemical modifications on the biosorbent properties including washing, alkali saponification, concentration of cross-linking reagent and temperature were investigated. Influence of pH of solution, initial Cd(II) concentration, shaking time and solid/liquid ratio on the removed of Cd(II) by different biosorbents were also studied.

## 2. Materials and methods

### 2.1. Adsorbent preparation

#### 2.1.1. Raw orange peel

The orange was washed with water. The crude orange peel (hereafter, abbreviated as OP) was dried in a convection oven at 50 °C for 72 h. Then ball-mill was utilized to turn dried orange peel into smaller particles of approximate size between 0.1 and 0.2 mm which were used in our experiments. Its average pore diameter was 30.5 Å and specific surface area was 128.7 $\text{m}^2\,\text{g}^{-1}$ (BET surface and pore volume was measured on a Quantachrome NOVA 1000).

#### 2.1.2. Washed with iso-propyl alcohol

Twenty grams of OP and 80% iso-propyl alcohol were put together into a flask and were stirred for 24 h at room temperature and then rinsed with 80% iso-propyl alcohol for three times. At last it was washed with distilled water until the filtrate was colorless. Thereafter, the filter residue was dried in an oven at 50 °C for 24 h. Finally, 10.5 g of adsorbent were obtained, hereafter abbreviated as PA1. In order to reduce the cost, another sample was obtained through the same pretreatment by substituting 80% iso-propyl alcohol with 20% iso-propyl alcohol, hereafter abbreviated as PA2.

#### 2.1.3. Modified with alkali saponification

Ten grams PA2 were taken in the beaker together with 200 mL 0.1 $\text{mol}\,\text{L}^{-1}$ NaOH and were stirred for 2 h at room temperature. After filtered, the sample was washed with distilled water until pH was neutral. The filter residue was dried in an oven at 50 °C for 24 h. Finally, 7.2 g of sample were obtained, hereafter abbreviated as SOP.

#### 2.1.4. Modified with citric acid

Ten grams PA2 together with 200 mL 0.1 $\text{mol}\,\text{L}^{-1}$ citric acid in the beaker were stirred for 2 h at room temperature, and then filtered. The sample was cleaned with distilled water until pH was neutral. The filter residue was dried in an oven at 50 °C for 24 h. Finally, we got 7.3 g product, hereafter abbreviated as CA1. Another sample was obtained by the above pretreatment only with one change of 0.6 $\text{mol}\,\text{L}^{-1}$ citric acid instead of 0.1 $\text{mol}\,\text{L}^{-1}$ citric acid, hereafter, abbreviated as CA2.

#### 2.1.5. Modified with citric acid after alkali saponification

Ten grams SOP were mixed with 70 mL 0.1 $\text{mol}\,\text{L}^{-1}$ citric acid in the beaker and stirred for 2 h at 80 °C. The acid/peel slurry was dried overnight at 50 °C in an oven and filtered subsequently. The dried sample was washed with distilled water until pH was neutral. The filter residue was dried in an oven for 24 h at 50 °C. Finally, we got 7.34 g product, hereafter abbreviated as $0.1\text{SCA}_{80}$. Other samples were obtained by the above pretreatment with only one change in adopting 0.3, 0.6 or 0.9 $\text{mol}\,\text{L}^{-1}$ citric acid instead of 0.1 $\text{mol}\,\text{L}^{-1}$ citric acid, respectively, hereafter, abbreviated as $0.3\text{SCA}_{80}$, $0.6\text{SCA}_{80}$, $0.9\text{SCA}_{80}$.

Ten grams SOP were mixed with 70 mL 0.6 $\text{mol}\,\text{L}^{-1}$ citric acid in the beaker and stirred for 2 h at 25, 50, 80 and 120 °C, respectively. The acid/peel slurry was dried overnight at 50 °C in an oven and filtered subsequently. The dried sample was washed with distilled water until pH was neutral. The filter residue was dried in an oven for 24 h at 50 °C. Hereafter, products were abbreviated as $0.6\text{SCA}_{25}$, $0.6\text{SCA}_{50}$, $0.6\text{SCA}_{80}$ and $0.6\text{SCA}_{120}$, respectively.

### 2.2. Biosorption experiments

In this study, all chemical reagents used were analytical grade and distilled water was adopted to prepare all the solutions. Meanwhile, In order to adjust the environmental parameters, 0.1 M NaCl was used to control the ionic strength and hexamethylene tetramine buffer solution was used for keeping proton balance. Stock metal solution was prepared by dissolving corresponding halide of 25 mL 0.1 M NaCl and 25 mL hexamethylene tetramine buffer solution (pH 6.0) and diluting quantitatively to a volume of 250 mL. The pH of each solution was adjusted with 0.1 M NaOH and 0.1 M HCl.

All of the adsorption tests were carried out batch wise, 0.025 g of dried adsorbent was taken into a conical flask together with a 15 mL portion of corresponding aqueous solution. The flasks were incubated in a rotary shake at room temperature. Solution samples were filtered through filter paper. The concentrations of cadmium ion were determined by standard EDTA titration, 0.1% Xylenol orange was chosen as indicator and 30% hexamethylene tetramine was used as buffer solution. The pH values of the aqueous solution were measured with a pHs-3C model acidity meter (made in China).

### 2.3. Data evaluation

The amount of adsorption was calculated based on the difference between the initial ($C_\text{i}$, $\text{mol}\,\text{L}^{-1}$) and final concentration ($C_\text{e}$, $\text{mol}\,\text{L}^{-1}$) in every flask, as follows:

$$q = \frac{(C_\text{i} - C_\text{e})V}{W} \qquad (1)$$