

## Enhancement of the adsorption of cadmium by modified orange peel with sodium hydroxide and ethyl alcohol

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**Keywords:** adsorption; cadmium ion; modified; orange peel

**Abstract.** The aim of this work was to modify orange peel with sodium hydroxide and ethyl alcohol, and optimize the modified conditions and the adsorption parameters. The effects of various parameters including NaOH solution volume, NaOH solution concentration, ethyl alcohol volume, reaction time, reaction temperature, pH and Cd<sup>2+</sup> solution initial concentration on the adsorption of Cd<sup>2+</sup> were investigated detailedly. The NaOH solution volume, NaOH solution concentration and ethyl alcohol volume had strong effects on the adsorption of Cd<sup>2+</sup> and their optimum values were determined as 25 mL, 24 g/L and 35 mL, respectively. The effects of reaction time and reaction temperature were not very significant and the appropriate values were determined as 10 min and 30°C, respectively. The pH and initial concentration of Cd<sup>2+</sup> solution were had great influences on the removal efficiency of Cd<sup>2+</sup>. The removal efficiency of Cd<sup>2+</sup> on modified orange peel had reached up to 98.4% when the initial concentration of Cd<sup>2+</sup> solution was 200 mg/L and the pH of Cd<sup>2+</sup> solution was 5.0, which was 4.6 times greater compared with that of pristine orange peel. The results showed this chemical modification of orange peel had enhanced effectively its adsorption capacity of cadmium.

### Introduction

The release of hazardous metal ions into the environment is still large and even increasing, resulting in a serious environmental issue. It is well known that these metal ions are significantly poisonous to human beings, include lead, cadmium, copper, zinc and nickel, etc. Currently the conventional methods for hazardous metal ions removal from aqueous solutions include chemical precipitation, evaporation, electrochemical treatment, membrane technology and the use of ion exchange resins, which are expensive and sometimes ineffective, especially in the case of the metal ions dissolved in large volumes of solution at relatively low concentrations[1].

Adsorption is the most effective, widely and economic used method for removal of different pollutant. It is well known that the adsorbent plays a very important role in the process of adsorption. In recent years, much attention has been given towards use of biological materials, including algae, bacteria, fungi, agricultural by-products and residues as adsorbents to remove toxic metal ions from aqueous solution by adsorption. Among these materials, agricultural by-products and biomass are relatively cheap. However, their adsorption capacity in nature is still low and the direct use as adsorbents can also bring several problems, such as high chemical oxygen demand and biological chemical demand as well as total organic carbon. To overcome such problems, chemical modification of adsorbents has been used as a technique for improving physical and chemical properties of them and enhancing their adsorption capacity[2]. Different kinds of biosorbent materials, such as chemically modified sugarcane bagasse and chemically modified jute fibers, have been reported for adsorption of different metal ions[3,4].

Orange peel as one of processing wastes possess little economic value and creates serious disposal problems[5]. It is mostly composed of cellulose, pectin, hemicellulose, lignin, chlorophyll pigments and other low molecular weight hydro-carbons. Many of these contain several functional groups, including carboxylic and phenolic acid groups that can be likely to form stable complexes with most of metal ions, which make the orange peel a potential adsorbent material[1,6,7].

This study aimed at preparation of a modified orange peel as an adsorbent by dealing with sodium hydroxide and ethyl alcohol, with the objective to detailedly investigate the effect of various parameters including NaOH solution volume, NaOH solution concentration, ethyl alcohol volume,

reaction time, reaction temperature, pH and  $\text{Cd}^{2+}$  solution initial concentration on the adsorption of  $\text{Cd}^{2+}$ , which is a hazardous metal ion for living systems.

## Experimental

### Instrumentation

An Analytik Jena ContrAA 700 High Resolution Continuum Source Atomic Absorption Spectrometer (Analytik Jena, Berlin, Germany) had been used for all measurements in this work. This spectrometer consists of a high-intensity xenon short-arc lamp, a high-resolution double echelle monochromator (DEMON) and a chargecoupled device (CCD) array detector[8-12]. The primary resonance line for Cd at 228.8018 nm was used for determination. The optimized determination conditions were shown in Table 1.

Table 1 Determination conditions of HR-CS FAAS

Flame type	Burner type	Spectr.range	Fuel flow (L/h)	Burner height (mm)
$\text{C}_2\text{H}_2$ -air	100mm	200	50	6

### Chemicals

All chemicals used in this study were of pure analytical grade and purchased from Chinese Medicine Group Chemical Reagent Co., Ltd, unless otherwise mentioned.  $\text{Cd}^{2+}$  solutions for drawing calibration curve were prepared with deionized water by serial dilution of the stock solutions with 100 mg/L (National Chemical Reagent Company, Beijing, China). The working solution (50-500 mg/L) of  $\text{Cd}^{2+}$  were prepared by dissolving cadmium sulfate in deionized water. The working solution pH was adjusted to the desired values by adding small amount of hydrochloric acid or sodium hydroxide.

### Modification of the orange peel

The pristine orange peel was carefully washed with deionized water to remove particulate material from their surfaces and dried at 60°C inside a convection oven for 24 h. The dried orange peel was crushed and sieved through a No. 50 mesh, obtaining uniform particles sized 0.335 mm after it was cooled. The obtained product was named as OP for further adsorption study and stored in a desiccator.

About 5 g of OP were taken into 100 mL conical flask with a mixture of 35 mL ethyl alcohol and 25 mL NaOH solution (24 g/L). The flask was shaken vigorously in a thermostated shaker at a speed of 160 rpm for 10 min at 30°C. After decantation and filtration, the treated biomass was washed with distilled water to remove excess alkali, salt and any other soluble substances until the solution reached a neutral pH value around 7.0, and then freeze-dried into a spongelike material inside a vacuum freeze-drying equipment. This dried product was prepared and abbreviated as MOP hereafter, and stored in a desiccator for further batch adsorption experiments after being crushed and sieved.

### Adsorption experiments

Experiments were carried out by mixing dried sorbents with working solution of  $\text{Cd}^{2+}$ . 200 mg of MOP were taken into 100 mL conical flask with 40 mL working solution (500 mg/L, pH 5.0) of  $\text{Cd}^{2+}$ . The flask was shaken vigorously in a thermostated shaker at a speed of 160 rpm for 2 h at 30°C to ensure that the adsorption of  $\text{Cd}^{2+}$  had very approached the equilibrium, removed and filtered for measurement of residual  $\text{Cd}^{2+}$  concentration afterwards.

The initial and equilibrium concentrations of  $\text{Cd}^{2+}$  were measured by HR-CS FAAS. The removal efficiency of  $\text{Cd}^{2+}$  was determined by using the following equation:

$$RE = (c_i - c_e) / c_i \times 100 \quad (1)$$

where  $RE$  (%) represents the removal efficiency of  $\text{Cd}^{2+}$  at equilibrium;  $c_i$  and  $c_e$  (mg/L) are the initial and equilibrium concentrations of  $\text{Cd}^{2+}$ , respectively.

## Results and discussion

### Effect of NaOH solution volume

The effect of NaOH solution volume was studied in the range 0-45 mL. Fig. 1. showed the influence of NaOH solution volume on the adsorption of  $\text{Cd}^{2+}$  in which the other experimental variables remained constant. The results showed that the optimum NaOH solution volume, 25 mL, used for the rest of this work in order to achieve the optimal modified conditions of OP.

### Effect of NaOH solution concentration

The effect of NaOH solution concentration was studied in the range 0-36 g/L. Fig. 2. showed the influence of NaOH solution concentration on the adsorption of  $\text{Cd}^{2+}$ . The results showed that the optimum NaOH solution concentration, 24 g/L, used for the rest of this work in order to achieve the optimal modified conditions of OP.

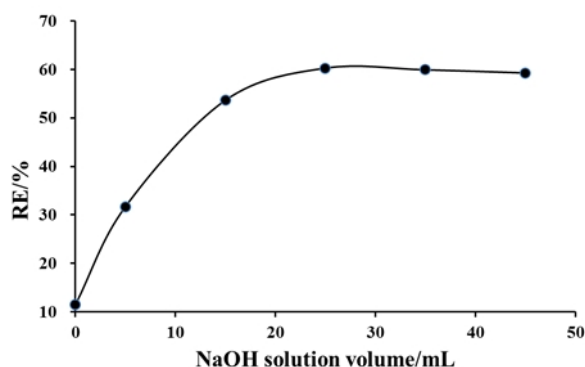


Fig. 1. Effect of NaOH solution volume on adsorption

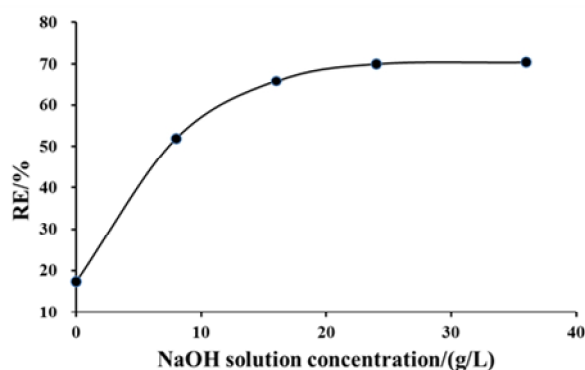


Fig. 2. Effect of NaOH solution concentration on adsorption

### Effect of ethyl alcohol volume

The effect of ethyl alcohol volume was studied in the range 0-45 mL. Fig. 3. showed the influence of ethyl alcohol volume on the adsorption of  $\text{Cd}^{2+}$ . The results showed that the optimum ethyl alcohol volume, 35 mL, used for the rest of this work in order to achieve the optimal modified conditions of OP.

### Effect of reaction time

The effect of reaction time was studied in the range 5-60 min. Fig. 4. showed the influence of reaction time on the adsorption of  $\text{Cd}^{2+}$ . The results showed that the optimum reaction time was 10 min and the effect of reaction time was not very significant. An appropriate reaction time, 10 min, was used for the rest of this work in order to achieve the optimal modified conditions of OP.

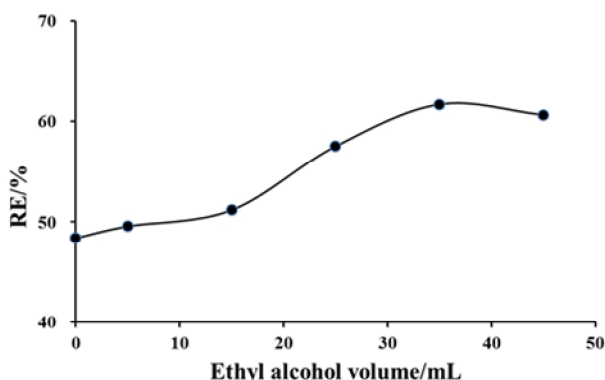


Fig. 3. Effect of ethyl alcohol volume on adsorption

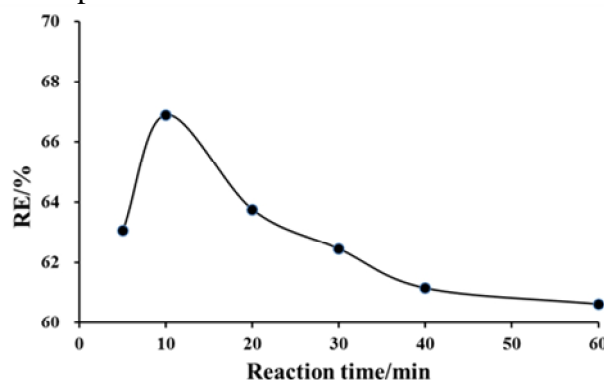


Fig. 4. Effect of reaction time on adsorption

### Effect of reaction temperature

The effect of reaction temperature was studied in the range 15-75°C. Fig. 5. showed the influence of reaction temperature on the adsorption of  $\text{Cd}^{2+}$ . The results showed that the optimum reaction temperature was 15°C and the effect of reaction temperature was not very significant. In order to facilitate the modified operation, an appropriate reaction temperature, 30°C, was employed for the rest of this work in order to achieve the optimal modified conditions of OP.

### Effect of pH

$\text{Cd}^{2+}$  solution pH was varied from 1.0 to 7.0. Fig.6. showed the influence of  $\text{Cd}^{2+}$  solution pH on the adsorption of  $\text{Cd}^{2+}$ . The results showed that the removal efficiency of  $\text{Cd}^{2+}$  increased as pH increased from 1.0 to 5.0 and then approximately trended to be stable. Hence, the optimal pH, in the range 5.0-7.0, was used for the rest of this work in order to achieve the optimal adsorption conditions of MOP.

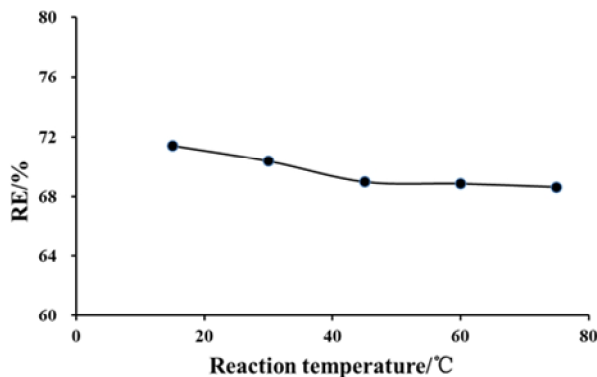


Fig.5. Effect of reaction temperature on adsorption

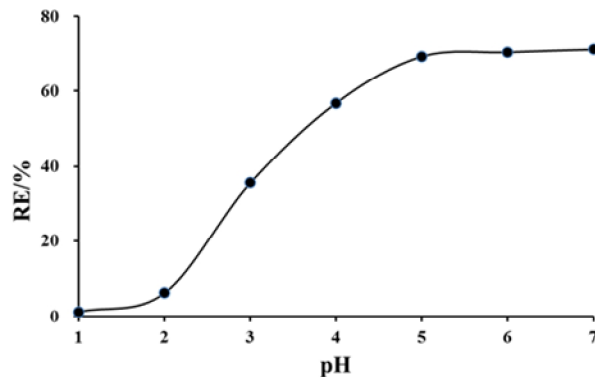


Fig.6. Effect of pH on adsorption

### Effect of $\text{Cd}^{2+}$ solution initial concentration

$\text{Cd}^{2+}$  solution initial concentration was varied from 50 to 500 mg/L. Fig.7. showed the influence of the initial concentration on the adsorption of  $\text{Cd}^{2+}$ . The results showed that the removal efficiency of  $\text{Cd}^{2+}$  approximately trended to be stable in the range 50-200 mg/L and then decreased by degrees as initial concentration increased from 200 to 500 mg/L. Hence, the removal efficiency of  $\text{Cd}^{2+}$  had reached up to 98.4% when the initial concentration of  $\text{Cd}^{2+}$  solution was less than 200 mg/L and the pH of  $\text{Cd}^{2+}$  solution was 5.0.

### Effect of modification

Adsorption capacity of OP and MOP was studied in 200 mg/L  $\text{Cd}^{2+}$  and pH 5.0. Fig.8. showed the influence of the modification with sodium hydroxide and ethyl alcohol on the adsorption of  $\text{Cd}^{2+}$ . The results showed that the removal efficiency of  $\text{Cd}^{2+}$  on MOP was 98.4%, which was 4.6 times greater compared with that of OP (21.5%).

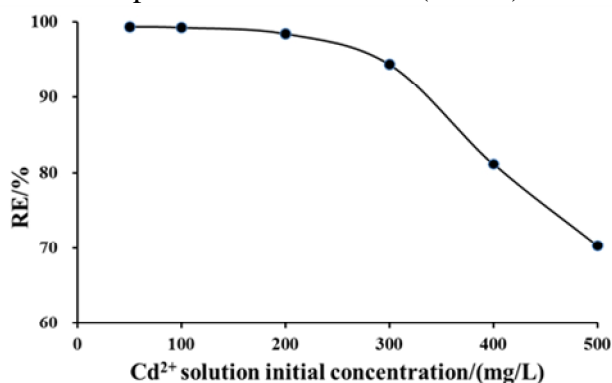


Fig.7. Effect of initial concentration on adsorption

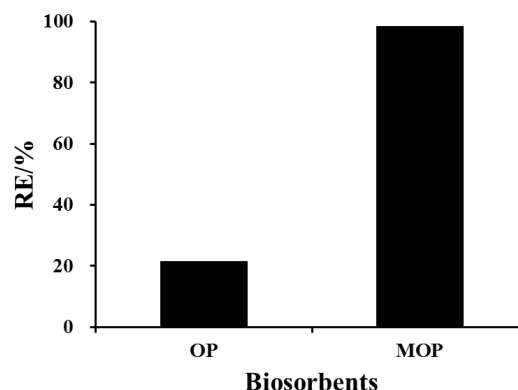


Fig.8. Adsorption capacity of OP and MOP

## Conclusions

OP was chemically modified with sodium hydroxide and ethyl alcohol, obtaining MOP as a novel biosorbent. The NaOH solution volume, NaOH solution concentration and ethyl alcohol volume had strong effects on the adsorption of  $\text{Cd}^{2+}$  and their optimum values were determined as 25 mL, 24 g/L and 35 mL, respectively. The effects of reaction time and reaction temperature were not very significant and the appropriate values were determined as 10 min and 30°C, respectively. The pH and initial concentration of  $\text{Cd}^{2+}$  solution were had great influences on the removal efficiency of

$\text{Cd}^{2+}$ . The removal efficiency of  $\text{Cd}^{2+}$  on MOP had reached up to 98.4% when the initial concentration of  $\text{Cd}^{2+}$  solution was 200 mg/L and the pH of  $\text{Cd}^{2+}$  solution was 5.0, which was 4.6 times greater compared with that of OP.

## Acknowledgements

This work was financially supported by the Practice Innovation Training Program of Students in Colleges and Universities in Jiangsu (No. xc2014059) and Open Project Program of Jiangsu Key Laboratory of Food Resource Development and Quality Safety, Xuzhou Institute of Technology (No. SPKF201317).

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