Optimization of process parameters of chemically modified orange peel for Pb^{2+} removal from aqueous solution

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Keywords: optimize; chemically modified; orange peel; orthogonal experiment

Abstract. The aim of this work was to chemically modify orange peel with ethyl alcohol, sodium hydroxide and calcium chloride, and optimize the modified process parameters through the orthogonal experimental design. The effects of various parameters on the removal efficiency of Pb^{2+} were investigated detailedly, including ethyl alcohol volume, NaOH solution volume, NaOH solution concentration and $CaCl_2$ solution volume. According to the results of the orthogonal experiments, the best levels for this four factors were obtained through a $L_9(3^4)$ matrix analysis, as follows: ethyl alcohol volume was 20 mL, NaOH solution volume was 20 mL , NaOH solution concentration was 30 g/L and $CaCl_2$ solution volume was 5 mL. The results were researched by the range analysis and showed that the NaOH solution concentration had the most significant impact on the removal efficiency of Pb^{2+}, whereas the ethyl alcohol volume had the least impact. The removal efficiency of Pb^{2+} of chemically modified orange peel from aqueous solution had reached up to 93.41% in the optimum levels, which showed this chemical modification of orange peel had enhanced effectively its removal capacity of Pb^{2+} from aqueous solution.

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[1,2]. 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[3].

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[4]. 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[5,6].

Orange peel as one of processing wastes possess little economic value and creates serious disposal problems[7]. 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[3,8,9].

This paper aimed at preparation of a modified orange peel as an adsorbent for Pb^{2+} removal by dealing with ethyl alcohol, sodium hydroxide and calcium chloride. The effects of chemically modified parameters were investigated detailedly and the orthogonal analysis was applied to

optimize this four modified process parameters (i.e. ethyl alcohol volume, NaOH solution volume, NaOH solution concentration and $CaCl_2$ solution volume).

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[10-13]. The primary resonance line for Pb at 283.306 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)
C_2H_2-air	100mm	200	65	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. Pb^{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 (100-1000 mg/L) of Pb^{2+} were prepared by dissolving lead nitrate 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 20 mL ethyl alcohol, 20 mL NaOH solution (30 g/L) and 5 mL $CaCl_2$ solution (100 g/L). The flask was shaken vigorously in a thermostated shaker at a speed of 160 rpm for 5 h 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 CMOP 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 Pb^{2+}. 200 mg of CMOP were taken into 100 mL conical flask with 40 mL working solution (1000 mg/L, pH 5.0) of Pb^{2+}. The flask was shaken vigorously in a thermostated shaker at a speed of 160 rpm for 2 h at 30°C to ensur that the adsorption of Pb^{2+} had very approached the equilibrium, removed and filtered for measurement of residual Pb^{2+} concentration afterwards.

The initial and equilibrium concentrations of Pb^{2+} were measured by HR-CS FAAS. The removal efficiency of Pb^{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 Pb^{2+} at equilibrium; c_i and c_e (mg/L) are the initial and equilibrium concentrations of Pb^{2+}, respectively.

2.5. Orthogonal design

In this study, the effects of chemically modified parameters on orange peel for Pb^{2+} removal were investigated through the orthogonal experimental design, the following four factors were analyzed: ethyl alcohol volume (factor A), NaOH solution volume (factor B), NaOH solution concentration

(factor C) and $CaCl_2$ solution volume (factor D). A $L_9(3^4)$ was employed to assign the considered factors as shown in Table 2 which is an orthogonal array of four factors and three levels. Nine trials were carried out to achieve the optimization process according to the $L_9(3^4)$. Range analysis was employed to reveal the optimal conditions of the modified process of orange peel for Pb^{2+} removal.

Table 2 Levels and factors affecting the modified process of orange peel

Level	Factors			
	A/mL	B/mL	C/(g/L)	D/mL
1	20	10	10	0
2	25	15	20	5
3	30	20	30	10

Results and discussion

Effect of ethyl alcohol volume

The effect of ethyl alcohol volume was studied in the range 0-30 mL. Fig.1. showed the influence of ethyl alcohol volume on the removal of Pb^{2+} in which the other experimental variables remained constant. The results showed that the removal efficiency of Pb^{2+} increased as the ethyl alcohol volume increased from 0 to 25 mL and then decreased slowly.

Effect of NaOH solution volume

The effect of NaOH solution volume was studied in the range 0-25 mL. Fig.2. showed the influence of NaOH solution volume on the removal of Pb^{2+}. The results showed that the removal efficiency of Pb^{2+} increased as the NaOH solution volume increased from 0 to 20 mL and then approximately trended to be stable.

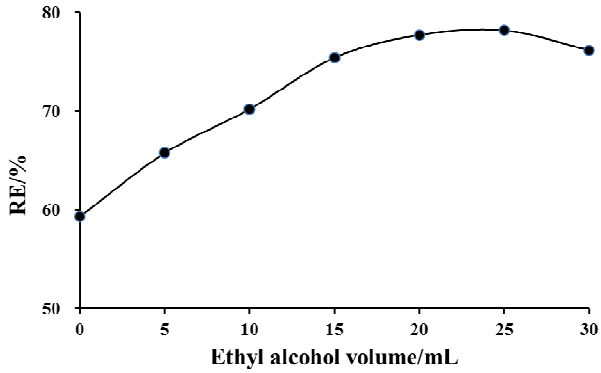

Fig.1. Effect of ethyl alcohol volume on removal of Pb^{2+}

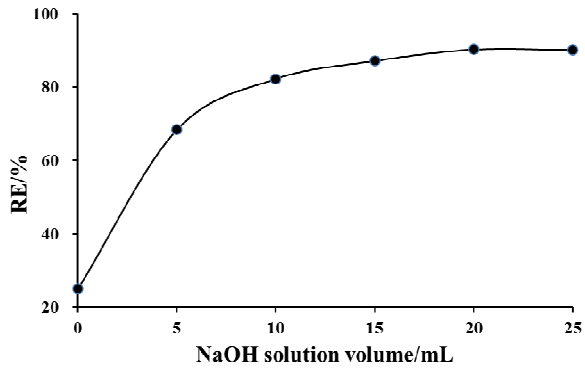

Fig.2. Effect of NaOH solution volume on removal of Pb^{2+}

Effect of NaOH solution concentration

The effect of NaOH solution concentration was studied in the range 0-50 g/L. Fig.3. showed the influence of NaOH solution concentration on the removal of Pb^{2+}. The results showed that the removal efficiency of Pb^{2+} increased as the NaOH solution concentration increased from 0 to 30 g/L and then approximately trended to be stable.

Effect of $CaCl_2$ solution volume

The effect of $CaCl_2$ solution volume was studied in the range 0-25 mL. Fig.4. showed the influence of $CaCl_2$ solution volume on the removal of Pb^{2+}. The results showed that the removal efficiency of Pb^{2+} increased as the $CaCl_2$ solution volume increased from 0 to 5 mL and then approximately trended to be stable.

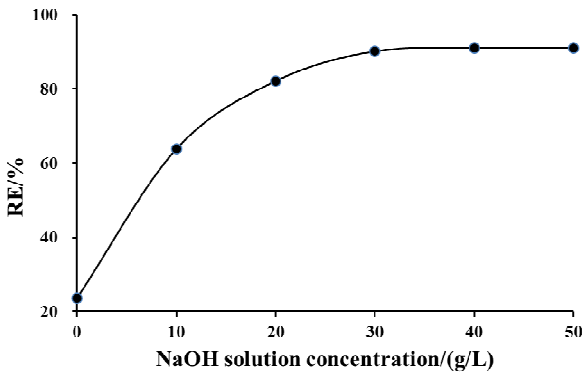

Fig.3. Effect of NaOH solution concentration on removal of Pb^{2+}

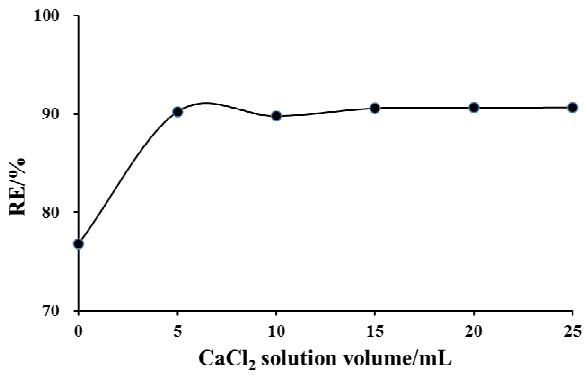

Fig.4. Effect of $CaCl_2$ solution volume on removal of Pb^{2+}

Range analysis

According to the $L_9(3^4)$ matrix, nine experiments were carried out and the results of the removal efficiency of Pb^{2+} were shown in Table 3. It shows that the range of the removal efficiency of Pb^{2+} varies from 48.53% to 91.28%. As mentioned that higher value for k_{ij} demonstrates that the corresponding level has a bigger effect on the removal efficiency of Pb^{2+}.

Therefore the best level for the four factors are as follows: ethyl alcohol volume was 20 mL, NaOH solution volume was 20 mL , NaOH solution concentration was 30 g/L and $CaCl_2$ solution volume was 5 mL, since the k_{ij} was the highest at these combination ($A_1B_3C_3D_2$) corresponding to that the removal efficiency of Pb^{2+} had reached up to 93.41%. Meanwhile, the value of R_j demonstrates the significance of the factor's influence and a larger R_j means the factor has a bigger impact on the removal efficiency of Pb^{2+}. In Table 3, the decreasing order $R_C > R_D > R_B > R_A$ indicates that the NaOH solution concentration had the most significant impact on the removal efficiency of Pb^{2+}, whereas the ethyl alcohol volume had the least impact.

Table 3 Results of the orthogonal test and range analysis data.

Level	Factors				RE/%
	A/mL	B/mL	C/(g/L)	D/mL	
1	1	1	1	1	48.53
2	1	2	2	2	84.35
3	1	3	3	3	91.28
4	2	1	2	3	68.75
5	2	2	3	1	77.99
6	2	3	1	2	69.91
7	3	1	3	2	84.93
8	3	2	1	3	58.93
9	3	3	2	1	72.22
k_1	74.72	67.40	59.12	66.25	
k_2	72.22	73.76	75.10	79.73	
k_3	72.02	77.80	84.73	72.99	
R	2.70	10.40	25.61	13.48	

Conclusions

OP was chemically modified with ethyl alcohol, sodium hydroxide and calcium chloride, obtaining CMOP as a novel biosorbent. This study uppermost proposed the optimization of modified process parameters of OP. The effects of various parameters on the removal efficiency of Pb^{2+} were investigated detailedly, including ethyl alcohol volume, NaOH solution volume, NaOH solution concentration and $CaCl_2$ solution volume. According to the results of the orthogonal experiments, the best levels for this four factors were obtained through a $L_9(3^4)$ matrix analysis, as follows: ethyl alcohol volume was 20 mL, NaOH solution volume was 20 mL , NaOH solution concentration was 30 g/L and $CaCl_2$ solution volume was 5 mL. The results were researched by the range analysis and

showed that the NaOH solution concentration had the most significant impact on the removal efficiency of Pb^{2+}, whereas the ethyl alcohol volume had the least impact. The removal efficiency of Pb^{2+} of CMOP from aqueous solution had reached up to 93.41% in the optimum levels.

Acknowledgements

This work was financially supported by the Entrepreneurial Innovation Training Program of Students in Xuzhou Institute of Technology (No. 201504), the Practice Innovation Training Program of Students in Colleges and Universities in Jiangsu (No. xcx2014059) 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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