Removal of chromium from aqueous solutions using modified lettuce leaves

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ABSTRACT

This article reports on an investigation into the ability of modified lettuce leaves to extract chromium ions from aqueous solutions. These exciting new materials were prepared via rapid (5 h) environmentally friendly synthesis routes avoiding any secondary pollution. The influence of pH, metal concentration, the adsorption of the added amount, and water temperature on the selectivity and sensitivity of the removal process was investigated. The maximum theoretical adsorption rate of modified lettuce leaves, evaluated by the Langmuir adsorption model, was 99.98%. The proposed method was applied in the determination of Cr^{6+} in a sample of aqueous solution and was validated by comparison with activated carbon.

Key words | biosorption, Cr^{6+}, modified lettuce, rate of adsorption, scanning electron microscopy (SEM)

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INTRODUCTION

The aim of this study was to evaluate the effectiveness of modified lettuce leaves in removing natural chromium from aqueous solutions.

Urbanization and industrialization of modern Chinese society has caused large-scale water-body pollution. Release of heavy metals into the biosphere by human activity has enormously increased, thereby impacting the geochemical cycle and food chain (Shanmugavalli *et al.* 2007). Heavy metals are known to be toxic, they can cause physiological disorders in organisms and phytotoxicity, even lead to death and the collapse of aquatic ecosystems (Ghata & Chaphekar 2000). Among all the toxic heavy-metals, chromium in its hexavalent form is known to cause wide-ranging health effects including mutagenic and carcinogenic risks (Park & Jung 2001).

Many physical, chemical and biological methods have been applied in the removal of chromium from river waste. The commonly used strategies include chemical precipitation (Zhang *et al.* 2008), ion exchange chromatography (Wang & Li 2012), liquid film methods (Li *et al.* 2011), and electrolytic methods (Zhang & Hu 2012), in which adsorption turn out to be very effective. However, the by-products generated during those processes may lead to secondary pollution. On the other hand, high cost and limited resource of raw materials make it difficult to absorb chromium.

Biological adsorption agents, as a new kind of heavy metal removal and recycling technology, are more likely to attract world-wide attention (Guo *et al.* 2012), especially in the treatment of low concentration metal wastewater, adsorption capacity and high-speed adsorption (Ahluwalia & Goval 2007). Most lettuce leaves are discarded in daily life, wasting of resources. So our research makes it into a biological absorbent, for absolutely lower cost.

MATERIALS AND METHODS

Adsorbent, reagent and equipment

The lettuce leaves were collected from a southern food market in Yuncheng. (This region is a centre for planting lettuce, producing a large number of discarded lettuce leaves every year.) The deionized water was made by deionizers. All of the reagents (potassium dichromate, sodium hydroxide, hydrochloric) were of AR grade.

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The metal ions were determined by atomic adsorption spectrometer TAS-990 made by Purkinje General Instrument Co, Ltd in Beijing.

Methods

Lettuce leaf slag preparation

On the basis of SHAO Huan-xia's carrot dietary fibre extraction process (Shao 2009), the technological preparation of the lettuce leaves, which served as a kind of biological absorbent, was as follows: They were initially softened by blanching treatment, the procedure of filtration was conducted, soaking in 2%NaOH. Dried lettuce leaves were first minced in a ball mill using a FRITSCH Pulverisette 6 for 25 min at 450 rpm. After pulverization, the lettuce leaf particles were sieved and the 40 μm fraction was selected for work.

Experimental design

Based on the present results of single-factor experiments (Xiang & Li 2007; Zhang & Qian 2009), the best operating conditions are obtained by the optimization of the key factors for the adsorption of Cr^{6+} from the aqueous solution sample.

Quadratic Orthogonal Regressive Rotation Design of five factors was applied in this study, including adsorbent addition, the concentration of nitrate solution, water time, pH value and temperature. Two influencing factors involving the zero level (Z_{0j}) and the time intervals Δj were worked out, according to the following equations:

$$Z_{0j} = \frac{Z_{1j} + Z_{2j}}{2} \tag{1}$$

$$\Delta j = \frac{Z_{1j} - Z_{2j}}{\gamma} \tag{2}$$

The code table of factors and levels (shown as Table 1) was made to demonstrate the gradients for various factors.

Table 1 | Code table of factors and levels

	X_1/(mg/l)	X_2/g	X_3	X_4/°C	X_5/h
−2	10	0.2	5	40	5.0
−1	20	0.3	6	50	5.5
0	30	0.4	7	60	6.0
1	40	0.5	8	70	6.5
2	50	0.6	9	80	7.0

The contrast experiment between lettuce leaf slag and activated carbon

Five solutions of different initial concentrations of Cr^{6+} (10, 30, 50, 70, 90 mg/L) were prepared, and each sample was taken as 20 ml, double, then adding lettuce leaf slag and activated carbon (0.2 g) respectively. The solution environment was regulated to pH (5) and temperature (40 °C) and this state was preserved for 5 hours, when supernatant was obtained. Next the supernatant was filtered and centrifuged. Finally, the metal ions were determined by atomic adsorption spectrometry.

The adsorption rate between lettuce leaf slag and activated carbon in five solutions of different initial concentration of Cr^{6+} were measured and compared:

$$\text{absorbance } (q) = \frac{(C_0 - C_1) \times V}{m} \tag{3}$$

$$\text{adsorption rate}/\% = \frac{(C_0 - C_1) \times 100}{C_0} \tag{4}$$

C_0: the initial concentration of metal ions before adsorption (mg/L); C_1: the balance concentrations of metal ions after adsorption (mg/L); V: the volume of the metal ions solution (L); m: the amount of added lettuce leaves slag (g) (Mondal 2010).

The adsorption isotherm of Cr^{6+}

The common isotherms to study the mechanism of the adsorption of heavy metal ions are those of Langmuir and Freundlich (Ren & Shi 2009). That of Langmuir (Langmuir 1918) is

$$\frac{C}{q} = \frac{C}{q_m} + \frac{1}{q_{m^b}} \tag{5}$$

That of Freundlich (Freundlich 1906; Bellot & Condoret 1993; Iqbal *et al.* 2009) is

$$q = KC_n \tag{6}$$

C: adsorption equilibrium concentration (mg/L); q: adsorption quantity (mg/g); q_m: saturated extent of adsorption (mg/g); b: adsorption equilibrium constant; K and n ($n < 1$): the constant at a certain temperature.

Data processing

The data were processed by Excel, SAS and DPS programs.

RESULTS AND ANALYSIS

The establishment of the regression equation

According to experimental results obtained by Quadratic and Orthogonal Regression and Rotation Combination, we obtained the following regression equations (X_1: concentrations of the solution; X_2: added amount; X_3: pH; X_4: temperature; X_5: time; Y: the adsorption rate):

$$\begin{aligned} Y = {} & 82.48910 + 7.98125X_1 - 3.35375X_2 \\ & + 1.40625X_3 + 1.39292X_4 - 2.73958X_5 - 5.06365X_1^2 \\ & - 3.11740X_2^2 - 2.53115X_3^2 - 1.86365X_4^2 + 2.17885X_5^2 \\ & + 0.07812X_1X_2 - 2.20312X_1X_3 - 3.39062X_1X_4 \\ & + 0.32812X_1X_5 - 0.73437X_2X_3 - 2.60937X_2X_4 \\ & + 1.04687X_2X_5 + 1.73437X_3X_4 - 0.79687X_3X_5 \\ & + 0.82182X_4X_5 \end{aligned} \tag{7}$$

The significance test and reconstruction of the quadratic regression model

For the validity of the regression model, testing effectiveness of fit has been done on the regression equation $F_1 = 3.21429 < F_{0.01(6,9)} = 5.80$ (Table 2). It shows that there are

Table 2 | Analysis of variance of results from quadratic orthogonal rotation combination test

Source of variance	SS	df	MS	F	P
X_1	1528.8085	1	1528.8085	38.7553	0.0001[b]
X_2	269.9433	1	269.9433	6.8431	0.0195[a]
X_3	47.4609	1	47.4609	1.2031	0.29
X_4	46.5652	1	46.5652	1.1804	0.2944
X_5	180.1276	1	180.1276	4.5662	0.0495[a]
X_1^2	820.4963	1	820.4963	20.7996	0.0004[b]
X_2^2	310.981	1	310.981	7.8834	0.0133[a]
X_3^2	205.0144	1	205.0144	5.1971	0.0377[a]
X_4^2	111.1416	1	111.1416	2.8174	0.114
X_5^2	151.917	1	151.917	3.8511	0.0685[a]
X_1X_2	0.0977	1	0.0977	0.0025	0.961
X_1X_3	77.6602	1	77.6602	1.9687	0.1809
X_1X_4	183.9414	1	183.9414	4.6629	0.0474[a]
X_1X_5	1.7227	1	1.7227	0.0437	0.8373
X_2X_3	8.6289	1	8.6289	0.2187	0.6467
X_2X_4	108.9414	1	108.9414	2.7617	0.1173
X_2X_5	17.5352	1	17.5352	0.4445	0.5151
X_3X_4	48.1289	1	48.1289	1.2201	0.2868
X_3X_5	10.1602	1	10.1602	0.2576	0.6192
X_4X_5	10.9727	1	10.9727	0.2782	0.6056
Orthogonal	4140.245	20	207.0122	$F_2 = 5.24776$	0.0004
Residual	591.716	15	39.4477		
Simulant	403.4429	6	67.2405	$F_1 = 3.21429$	0.0311
Error	188.273	9	20.9192		
Sum	4731.961	35			

[a]Significant difference at the 0.05 level.
[b]Significant difference at the 0.01 level.

some unknown factors influencing the experimental effect, but $F_2 = 5.24776 > F_{0.01(20,15)} = 3.37$. The test of significance of regression is remarkable; it shows that the five factors which we have investigated have a significant effect on the Cr^{6+} adsorption capacity of lettuce leaf slag.

Taking out the insignificant part of the Equation (7), we obtain the simplified regression equation as follows:

$$Y = 82.48910 + 7.98125X_1 - 3.35375X_2 - 2.73958X_5 - 5.06365X_1^2 - 3.11740X_2^2 - 2.53115X_3^2 + 2.17885X_5^2 - 3.39062X_1X_4 \quad (8)$$

Surface analysis of factors influencing interaction response

Regression equation showing that X_1X_4 has more significant influence

Under the conditions of other factors determining, when the temperature was constant, increasing concentration, the adsorption rate of lettuce leaf slag firstly increased and then decreased; the effect of lettuce leaf slag on the adsorption of chromium ions in aqueous solution showed a slow upward trend with increasing temperature, and the maximum adsorption rate of 98.76% was observed with a concentration of 50 mg/L and temperature of 40 °C. This indicates that in the interaction of the two factors, the impact of the role on the adsorption rate is relatively clear (Figure 1).

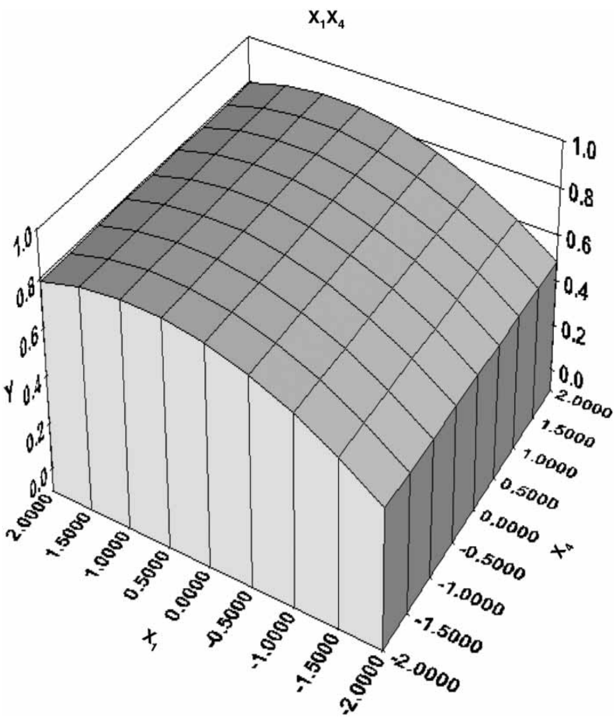

Figure 1 | The relationship between temperature and density shows that X_1X_4 had more significant influence. Under these favourable conditions, adsorption is maximal.

The optimal parameter combination for the lettuce leaf slag adsorption rate of Cr^{6+}

Following analysis, we concluded that the optimal operating conditions for the adsorption of Cr^{6+} by the abandoned lettuce leaves are pH of 7, temperature of 40 °C, time of 5 h, concentration of Cr^{6+} solution of 50 mg/L, and added amount lettuce leaves of 0.3 g, Under these conditions the experimental value ($Y = 98.76\%$) is close to the theoretical value ($Y = 99.98\%$), so the model is reasonable and credible.

The comparison of adsorption rate for Cr^{6+} between lettuce leaf slag and activated carbon

The slag adsorption rate for Cr^{6+} was better than activated carbon in general. It showed that within a certain range, the

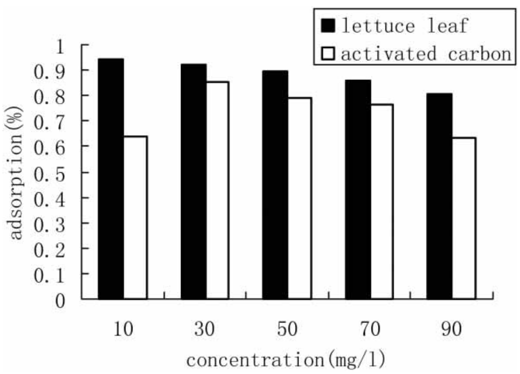

Figure 2 | Comparing slag with activated carbon, the modified lettuce leaf slag adsorption rate for chromium was better than activated carbon in general. Results represent the means of three independent experiments.

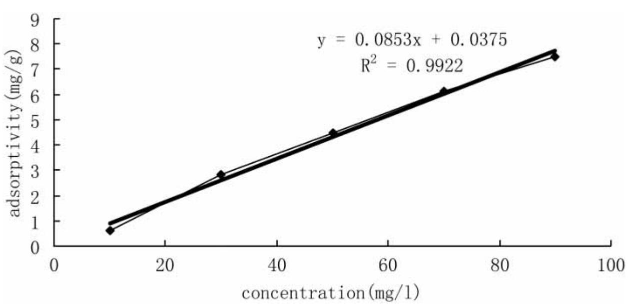

Figure 3 | The figure shows the relationship between the balance concentration of Cr^{6+} and adsorption at 40 °C. The adsorption isotherm is almost straight when the equilibrium concentrations are in the range 40–60 mg/L. Values are averages of three independent experiments.

adsorption effect of lettuce leaf slag on the adsorption of chromium ions is better than the activated carbon (Figure 2).

The adsorption mechanism is the key element in adsorption activity. The physical characters of activated carbon determine its capacity to absorb Cr^{6+}, however, the main ingredient of lettuce leaf slag is cellulose, which has a strong cleaning ability for heavy metals. Most importantly, cellulose in modified lettuce leaves enhances this ability.

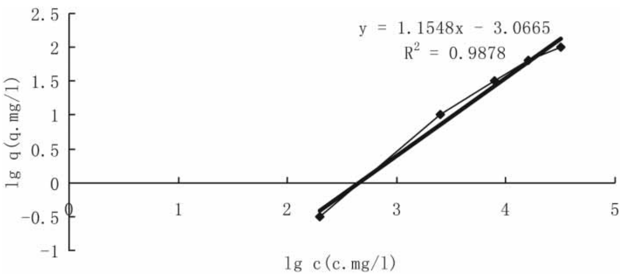

Figure 4 | The figure shows Freundlich isotherm plots for biosorption of chromium. Values are averages of three independent experiments.

For the same Cr^{6+}concentration, especially in a low concentration Cr^{6+} solution (10–100 mg/l), lettuce leaf slag had a more effective adsorption capacity than activated carbon.

The adsorption isotherm of Cr^{6+}

Adsorption isotherm of Cr^{6+} when the temperature was limited to 40 °C

The experimental data for chromium ions in lettuce leaf slag solution were analyzed employing Langmuir and Freundlich equilibrium isotherm models. The correlation coefficient for the Langmuir isotherm is presented in Figure 3, and the

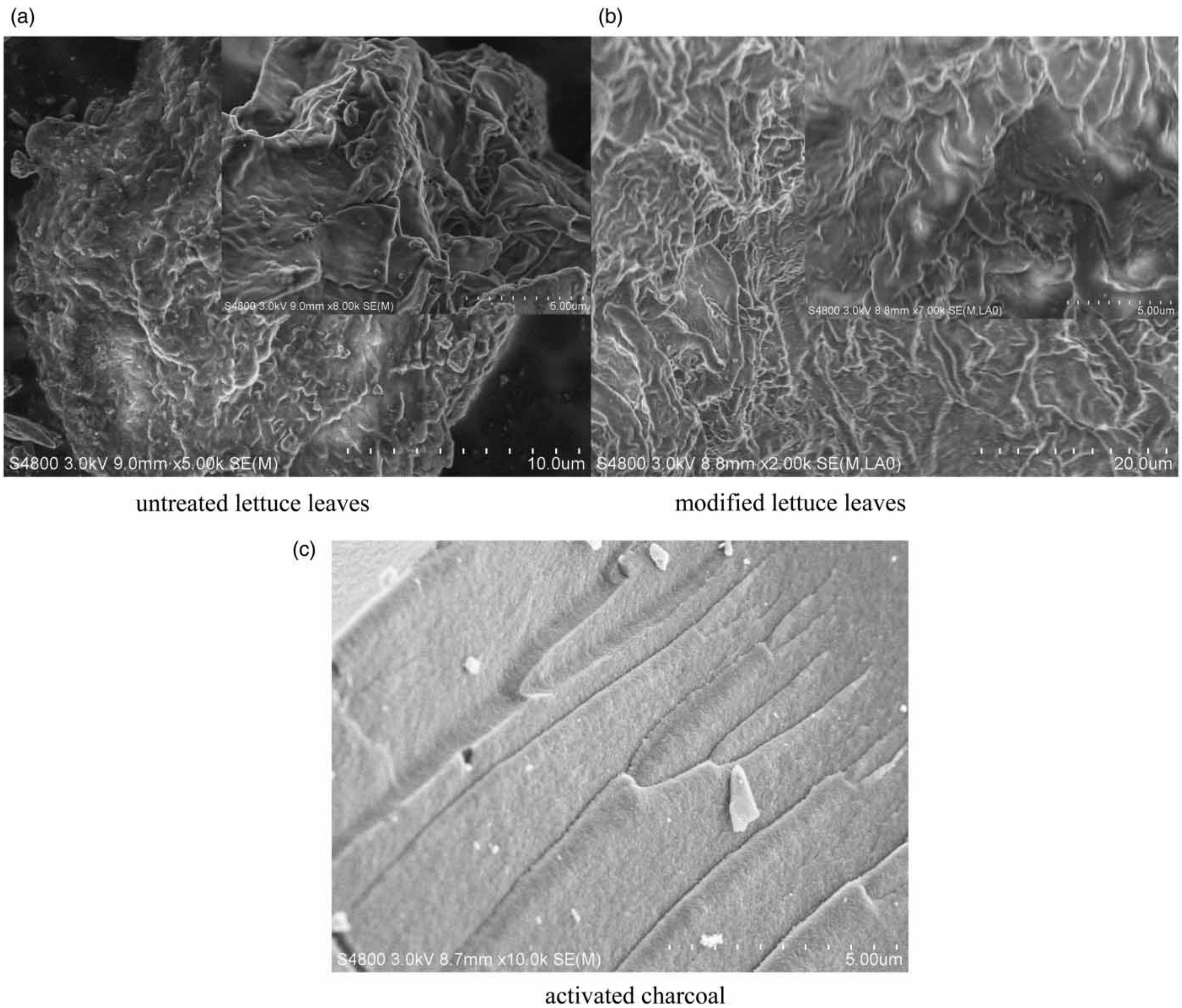

Figure 5 | The mainly structural changes of lettuce leaf slag after adsorption, and its similar loose structures to activated carbon.

correlation coefficient for the Freundlich isotherm is presented in Figure 4. The results show that biosorption is well described by the Langmuir isotherm equation.

Microscopic examination by scanning electron microscopy (SEM): results and analysis

As Figure 5 shows, modified lettuce leaves and activated carbon share a similar physical structure which is characterized by rough, unconsolidated porous and expensive surface area. The adsorption rate is increased due to this special structure.

DISCUSSION AND CONCLUSION

The adsorption capacity is comparable to results published by other authors (Miretzky & Fernandez Cirelli 2010), suggesting that the modified biosorbent has a great potential in removing heavy metals from wastewater. Evaporative concentration flame atomic adsorption spectrometry determines iron in water with manganese, copper, zinc, lead, and chromium.

The maximum adsorption rate of lettuce leaf slag was 99.98%, with pH of 7, at 40 °C, in a time of 5 h, at 50 mg/l concentration and an added amount of 0.3 g. These conditions have been validated by the measured value of 98.76%, coincident with the theoretical value. As we all know, this biomaterial is very attractive due to its low cost, and this study leads to the conclusion that lettuce leaves can be applied in removing metal ions from natural river waste. A Langmuir adsorption isotherm well describes the thermodynamic conditions of lettuce leaf Cr^{6+} adsorption. For the same Cr^{6+}concentration, especially in low concentration Cr^{6+} solution, lettuce leaf slag has a better effective adsorption capacity than activated carbon. As SEM images show, modified lettuce leaf slag has a rough, loose, porous surface.

We have gained some knowledge about adsorption mechanisms of biological absorbents in this paper. A non-toxic low-cost and effective biological absorbent will be developed and attract the world-wide attention.

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