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ARTICLE

Treatment of Chromium in Wastewater by using Loquat Leaves as Biosorbent

Ching-Hua Liao[1,2], Jer-Yuan Shiu[1,2]*, Chi-En Hung[3,4], Chih-Hung Wu[1,2], Ming-Zhong Liu[2]

[1] School of Resource & Chemical Engineering, Sanming University, FuJian, 365004, China
[2] Fujian Provincial Engineering Research Center of Mine Ecological Construction, Sanming, 365004, China
[3]Jiangsu Highwell Testing Technology co. LTD, Jiangsu, 223005, China
[4]School of Chemistry and Chemical Engineering, Huaiyin Normal University, Jiangsu, 223300, China

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A B S T R A C T

Heavy metal pollution generating from industries is a serious issue in China as it causes severe environmental pollution and health problems. Chromium is one of the common heavy metal appeared in wastewater of metal plating and processing industries and has to reduce its concentration to permissible levels before discharge by law. This study focused on removing chromium ion present in wastewater by using bioresource material loquat leaves as an adsorbent. The extent of adsorption of chromium ion was studied and found to be dependent on solution contact time with the adsorbent, particle size and dosage of the loquat leaves and chromium concentration. The result showed that the loquat leaves have a 70% efficiency in removing chromium ions. The experimental equilibrium biosorption data were analyzed by two widely used isotherms namely Langmuir, and Freundlich. The Langmuir isotherm model better fits the experimental data than the Freundlich isotherm model by high correlation coefficients R^2. The maximum monolayer capacity of loquat leaves was found to be 0.0201 mg/g for Chromium ions.

1. Introduction

Heavy metal pollution is a serious concern in China that wastewater originated from many industries such as mining, smelting, metal processing industries (Elhafez et al., 2017; Hegazi, 2013). Heavy metals in wastewater streams has become a significant problem that causes severe environmental pollution and harmful to human health (Taty-Costodes et al., 2005; Kadirvelu et al., 2001; Srivastava et al., 2006; Ali et al., 2018). To avoid health hazards and environmental problems, these harmful heavy metals must be removed from wastewater as much as possible (Lakherwal, 2014). Chromium (Cr) is one of the heavy metal ions in the above metal plating industries wastewater and has to reduce its concentration to permissible levels before discharge into water. Various methods can achieve removals of chromium ions from wastewater consist of precipitation, membrane filtration, ion exchange and adsorption (Chand et al., 1994; Das et al., 2008; Prakash et al., 2019). However, these methods are almost either expensive or ineffective, so need a method to replace all of these problems and treat the wastewater appropriately (Elhafez et al., 2017; Veglio et al., 1997). Consequently, it is extremely important to develop a simple, cheap, low cost effective, good bio-adsorption

* Corresponding author.
E-mail address: frankshiu@qq.com (Jer-Yuan Shiu)

efficiency's bioresource to remove the chromium in the wastewater and safeguard our future generations (Ullah et al., 2019).

There is a growing demand to find relatively efficient, low cost and easily available adsorbents for chromium adsorption, particularly if the adsorbents are the wastes or bioresource. The researchers were oriented toward low-cost adsorbents which are the agro wastes such as: the tree fern, green coconut shell powder, degreased coffee beans, orange waste, juniper bark, maize leaf, ulmus leaves, sugarcane bagasse, waste straw etc. (Hegazi, 2013; Mohan et al., 2002; Khan et al., 2001; Ayub et al., 1998; Ayub et al., 2001; Ayub et al., 2002). Because the bioresources have high porosity and large specific surface area, which can physically adsorb with some metal ions, some bioresources contain active substances such as tannin, which has a high metal ion binding capacity. Therefore, it can be directly used as a metal ion binding agent in wastewater (Ai-ping et al., 2007; Ma et al, 2003). The Loquat (Scientifically called Eriobotrya japonica) plant is belonging to the Rosaceae family and was originally grown in China. Loquat leaves are used to make tea and its fruits are widely used in medicine. As Loquat leaves are widely available in several sub-tropical countries in Asia, this could be used as a potential adsorbent to remove metal ions. Awwad and Salem (2014) were successfully used Loquat leaves as biosorbent for the removal of cadmium ions from aqueous solutions. Therefore, the present investigation is carried out to show the potential of biosorption of chromium on Loquat leaves. The effect of time, initial concentration of the chromium, adsorbent particle size and adsorbent dosage on the adsorption at room temperature is studied. The equilibrium data are fitted with Langmuir and Freundlich isotherms equations. Results from this study can be used to assess the utility of Loquat leaves for cadmium removal from water and industrial wastewaters (Awwad and Salem, 2014).

Nomenclature and abbreviation	
Cr	Chromium
SEM	Scanning Electron Microscope
EDS	Energy Dispersive Spectrometer
hr	hour
min	minutes

2. Materials and methods

2.1. Adsorbent

The bioresource raw Loquat leaves were collected from Sanming City, Fujian Province, China. After collection of leaves, they were thoroughly rinsed with water to remove dust and soluble material. Then it was allowed to dry at room temperature. The dried waste was grounded to a fine powder in a grinding mill and sieved to get 20, 50, 80 meshes (aperture 0.85mm, 0.30mm, 0.18mm) size fractions. The fine powder was then dried in an oven at 50 ºC for 48 hrs.

2.2. Preparation of Chromium ion solution and adsorption experiments

An adsorbate standard stock solution (1000 mg/L) of chromium is purchased from Beijing institute of non-ferrous metals Co. Ltd. This stock solution is used to make further diluted concentrations of interest with double distilled water. Batch adsorption experiments are carried out by shaking 100 mg of adsorbent (Loquat leaves powder) mixed with 10 mL of chromium solution of known concentration in 50 mL reagent bottles at room temperature in a rotatory mechanical shaker at 100 rpm. The effect of contact time, metal ion concentration, the effect of adsorbent dose and effect of adsorbent particle size are studied. The bottles are removed after the desired contact time and the filtrates are analyzed using atomic adsorption spectrophotometer (Beijing Beifen-Ruili Analytical Instrument (Group) Co., Ltd.). Double distilled water is used in preparing the stock solutions and also throughout the experimental analysis. Four samples of chromium ion concentrations varying from 10-80 mg/L were treated with 100 mg of the biosorbent.

After each system attains the equilibrium, the metal uptake capacity for each sample is calculated according to mass balance on the metal ion using

$$q_e = \left(\frac{C_i - C_e}{m}\right).v \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad [1]$$

$$\text{Biosorption percentage (\%)} = \left(\frac{C_i - C_e}{C_i}\right).\times 100 \quad \ldots. \quad [2]$$

where C_i and C_e are initial and equilibrium concentrations of chromium respectively, m is the mass of adsorbent and *V* is volume of solution in liters.

2.3. Adsorption Isotherms

Analysis of equilibrium data was important for the industrial application of biosorption since it gives information for comparison among different biomaterials under various operating procedures. Adsorption isotherm models were widely employed phenomena to examine the relationship between sorbed (Qe) and aqueous concentrations (Ce). Although a range of isotherm models were available to study the equilibrium data, of which the most popular Langmuir and Freundlich adsorption isotherms were employed for this study. The Langmuir isotherm model was used to estimate the maximum uptake values of chromium onto the biosorbent and the Freundlich isotherm was used to define the relationship between the uptake capacity and the residual concentration of chromium at equilibrium. The Langmuir and Freundlich isotherms were

$$q_e = Q^0 b C_e/(1+bC_e) \quad \ldots\ldots\ldots\ldots \quad [3]$$

$$q_e = K_f C_e^{1/n} \quad \ldots\ldots\ldots\ldots \quad [4]$$

Where q_e is the specific metal uptake, Q^0 the maximum monolayer sorption capacity (mgg^{-1}), *Ce* the equilibrium concentration in mgL^{-1}, *b* relates to the affinity of the sorbate for the binding sites expressed in Lmg^{-1}, K_f relates to the adsorption capacity and $1/n$ is the empirical parameter relating the adsorption intensity. The standard procedure was applied with SEM-EDS Analysis.

3. Results and discussion

3.1. Effect of time on chromium adsorption

The effect of agitation time on the adsorption of chromium from aqueous solution was investigated at a concentration of 10 mg/L. 100mg of the biosorbent Loquat leaves was added to 25 mL of the chromium solution in a 50mL reagent bottle and agitated at 80rpm in a rotary shaker with the temperature maintained at 27±0.5ºC. The biosorption capacity was recorded at different time intervals (1, 3, 5, 10, 30 and 60 min) and also the percentage of chromium adsorption was calculated. The percent biosorption efficiency of Loquat leaves at different time intervals are presented in Fig. 1. It can be seen from the figure that the percentage removal of metal ions increases with contact time starts from 1 minute (36 %) up to 10 minutes (70%), there after it decreases to 36% by 30 minutes and maintain equilibrium.

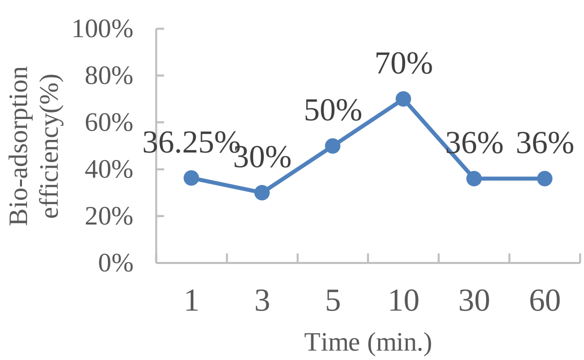


Fig. 1. the bio-adsorption efficiency of Cr at different time

3.2. Effect of particle size

At 27 ºC, the effect of particle size on the adsorption process was studied with 1 g Loquat leaves powder of various particles sizes >0.85mm, 0.85-0.30mm, 0.30-0.18mm, <0.18mm in 25 mL of 80 mg/L of chromium ion solution.

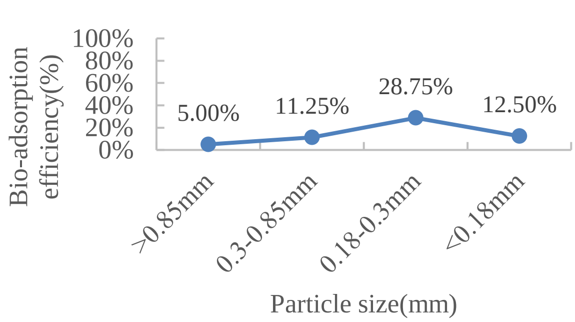
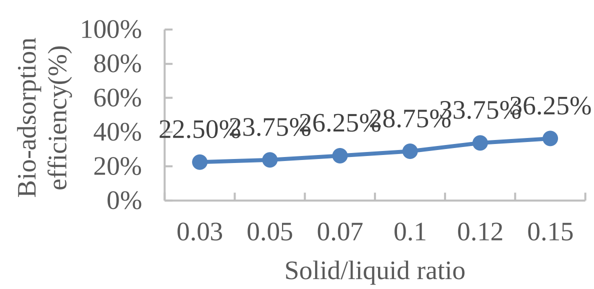


Fig. 2. the bio-adsorption efficiency of Cr at different particle size

The percent adsorption of chromium ions is 5.00, 11.25, 28.75 and 12.50 for the above particle sizes, respectively and the results are depicted in Fig. 2. The adsorption efficiency is increased with increasing particle size from >0.85mm to 0.30-0.18mm and decreases thereafter. Therefore, the adsorbent powder of 0.18 mm to 0.30 mm size appeared as good for adsorption of chromium ion.

3.3. Effect of adsorbent dose

To determine the effect of adsorbent dose, different amounts 0.1 to 1.5 g of loquat leaves were suspended in 10 mL of chromium solution in which the concentration of chromium is 80 mg/L under optimized conditions of contact time of 10 min and particle size 0.18 mm to 0.30 mm. The effect of the quantity of bioresource sample (Loquat leaves) on adsorption of chromium is presented in Fig. 3. From the figure, it is observed that percentage removal of chromium increased with the increase in adsorbent dose from 0.1 to 1.5 g. This is expected due to the fact that the higher dose of adsorbent in the solution results in greater availability of adsorption

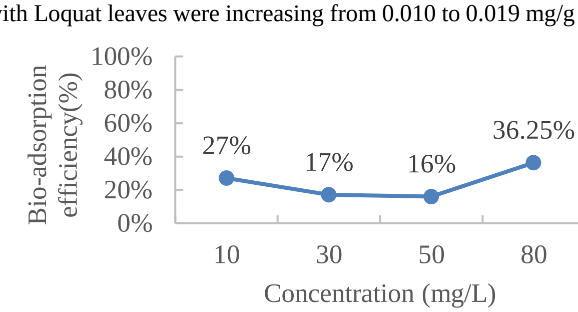


sites for the chromium ions. The maximum chromium ion removal efficiencies was 36.25% with Loquat leaves.

Fig. 3. the bio-adsorption efficiency of Cr at different solid/liquid ratio

3.4. Effect of chromium ion concentration and adsorption isotherms

To study the effect of the concentration of the chromium on the adsorption, the effect of different concentration of chromium such as 10, 30, 50, and 80 mg/L were added to the 100 mg of Loquat leaves powder at 27ºC, and the reaction was allowed to continue for 10 minutes. The aforementioned biosorption results are listed in Figure 4. From the figure, it is observed that, as the metal ion concentration increased the adsorptive capacity of the Loquat leaves powder increases. The adsorption capacity values with Loquat leaves were increasing from 0.010 to 0.019 mg/g with



the concentration. To elucidate the probable adsorption mechanism for this increase in adsorption behavior, adsorption isotherm models were used to interrogate the equilibrium data.

Fig. 4. the bio-adsorption efficiency of Cr at different concentration

The linearized forms of equations (3) and (4) were used to graphically represent the isotherms shown in Fig. 5. and Fig. 6. From the Langmuir and Freundlich isotherms plot, the calculated values of the characteristic parameters: Q^0, b, Kf and n as determined from the slope and intercept were summarized in Table 1, in addition to their relevant correlation coefficients for each model. The Langmuir isotherm describes the monolayer adsorption on a homogeneous surface with uniform adsorption energies for all binding sites. The Freundlich isotherm describes multilayer adsorption onto heterogeneous surfaces with the frequency of sites associated with the free energy of adsorption decreasing exponentially with the increase of the free energy. These two isotherms represent the data adequately and the experimental data is well fitted to both Langmuir and Freundlich with a correlation coefficient close to unity. The maximum monolayer adsorption capacity of Loquat leaves 0.021 mg/g.

Table 1
Langmuir and Freundlich adsorption constants for the adsorption of chromium ion on Loquat leaves.

Adsorbent	Q^0 (mg/g)	b (L/mg)	R^2	K_f	n	R^2
Loquat leaves	0.0201	3.96 $\times 10^{-5}$	0.993	0.00494	3.295	0.992

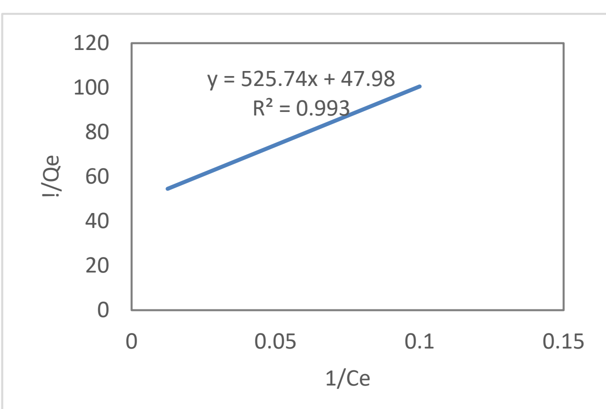


Fig. 5. Langmuir adsorption isotherm for adsorption of chromium ion on Loquat leaves

Fig. 6. Freundlich adsorption isotherm for adsorption of chromium ion on Loquat leaves

3.5. SEM-EDS Analysis

SEM images of the Loquat leaves before and after chromium ion adsorption were shown in Fig. 7. An examination of the SEM micrographs indicates the porous and heterogeneous surface area of the biosorbent. Comparison of these micrographs before and after chromium ion adsorption indicates that there is no significant change in the morphology of the surface of the biosorbents. The energy dispersion spectra confirms the presence of chromium ion adsorbed on Loquat leaves.

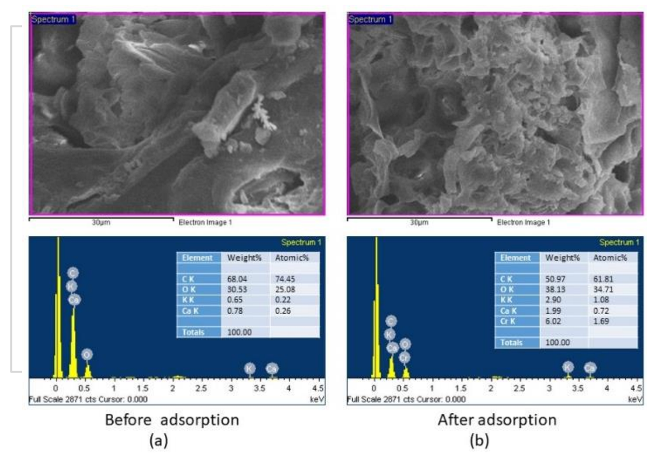


Fig. 7. SEM-EDS analysis of Cr adsorption by bioresource (loquat leaves): (a) before adsorption and (b) after adsorption.

4. Conclusions

In this study, Loquat leaves powder adsorbent is utilized to remove chromium ions present in aqueous solutions. The adsorption of chromium ions depends heavily on the amount of adsorbent, concentration of metal ion, contact time and particle size of the adsorbent. The optimum adsorption conditions were: 0.30-0.18mm size of Loquat leaves, 1.5 g dose of adsorbent, metal ion concentration 80 mg/L, and 10 minutes of contact time. Therefore, this research concludes that the Loquat leaves could adsorb metal ions present in aqueous solutions. The equilibrium adsorption data were correlated by Freundlich and Langmuir isotherm equations. The maximum adsorption capacity of Loquat leaves for chromium ions in this study is 0.0201 mg/g.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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