Ionic Strength Effect on Copper(II) Biosorption by *Folium camelliae* Biomass: Equilibrium Study and Dynamic Modelling in Membrane Reactor

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The removal of heavy metals by adsorption using biomaterials has been widely reported in the literature. The biosorption of copper(II) by the *Folium camelliae* was investigated a function of initial lead concentration, biosorbent concentration, temperature and pH, contact time and temperature was carried out. The nature of the possible biosorbent and metal ion interactions was examined by the FTIR technique. Adsorption equilibrium was observed within 1 h. Adsorption equilibrium data were well described by Langmuir isotherm model. The maximum adsorption capacity was 75.20 mg g^{-1} at 318 K and pH 4.4. From the Dubinin-Radushkevich model, the mean free energy was calculated as $12.1\text{--}15.8 \text{ kJ mol}^{-1}$ ranging from 285–318 K, indicating the adsorption was taken place by chemical ion-exchange. Thermodynamic parameters (ΔG° , ΔH° and ΔS°) were also evaluated. These parameters showed that the adsorption process was feasible, spontaneous and endothermic under studied conditions. Desorption experiments indicated that the fixed lead on the biomass was stable in common solutions except acid media. These results announced an excellent adsorption material and also strongly suggest us that tea plant must be kept away from lead pollution.

Key Words: Adsorption, *Folium camelliae*, Copper(II).

INTRODUCTION

Increasing industrialization brings with it the problems of removal of undesired and possibly toxic metals from chemical process effluent. Several toxic metals, which present in the waste water, such as cadmium, lead, zinc and copper cannot be degraded by biological and chemical processes¹. The discharge of non-essential nature of these metals into environment poses a severe threat to human and living creatures. In this condition, these metals are highly toxic non-essential elements that serve no known biological function. In addition, these metals tend to bioaccumulate and biomagnify in our food chain, which could be eventually consumed by human².

Traditional technologies for removal of heavy metal, including ionic exchange and precipitation are frequently inefficient and or expensive when applied for removal of metal ions in low concentrations. Several treatment processes have been developed over the years to remove heavy metals dissolved in the wastewater, such as chemical precipitation, chemical oxidation and reduction, ion exchange, solvent extraction and membrane filtration. However, these methods are either inefficient or expensive when heavy metals exist in low concentrations. Additionally, these methods may also create secondary pollution¹. Consequently, there is a dire need for new technologies or materials for heavy metal sequestration.

In recent years, many researchers have been investigating ideal adsorbents for heavy metal removal such as barley straw², *Mucor rouxii*³, *Antep pistachio* shells⁴, spent grain⁵, *Sphagnum* peat⁶, peanut husk⁷. All of these agricultural by-products have showed excellent biosorption behaviour.

Green tea originates from China. There are more than 1,600,000 hectare of *F. camelliae* gardens in China. Some scientists have done much job on various tea leaves modified or rinsed with hot water^{8,9}. But lead pollution is unavoidable during the tea processing and experiments conducted with pretreated material makes it difficult to get raw information on the susceptibility to metal pollution of fresh tea planting. Therefore, *F. camelliae* without any modification was used in our study based on triple purposes: (1) to probe the potential of *F. camelliae* as a low-cost substitute for conventional adsorbents with batch experiment method and spectral analysis; (2) to gain insight into whether the quality of tea product would be contaminated by lead owing to the common water and air pollution; (3) to give suggestions to tea planting.

EXPERIMENTAL

Folium camelliae was collected from Huaguo Mountain of China. The sample was properly cleaned with deionized water, dried at 333 K and finally ground to pass a 100-mesh sieve. The BET surface area was determined as $1.05 \text{ m}^2 \text{ g}^{-1}$ by

nitrogen adsorption isotherms measured at 77 K using a N₂ adsorption analyzer (Micromeritics ASAP 2020). Analytical grade reagents were used in all cases.

Batch adsorption experiments were carried out in capped conical flask (250 mL) at a specified temperature, by suspending 0.2 g of adsorbent in 100 mL of copper(II) solution at specified solution pH. The suspensions were mixed on a shaker with a constant agitation speed of 120 rpm. When finished, solid was separated and the filtrate was analyzed with an atomic absorption spectrometer (TAS-990, PGENERAL, China). The amount of copper(II) sequestered was calculated using mass balance equation.

RESULTS AND DISCUSSION

FTIR analysis: The FTIR spectra (Table-1) of dried unloaded *F. camelliae*, copper(II)-loaded biomass were recorded to obtain information on the nature of possible biomass-metal ion interactions.

Frequency (cm ⁻¹)		Association
Raw biomass	Lead(II) loaded biomass	
3419.55	3415.78	-OH, -NH stretching
2923.26	2924.45	C-H stretching
1646.40	1649.26	C=O chelate stretching, amide I band
1452.33	1454.08	C-CH ₃ asymmetric stretching
1146.81	1147.60	C-O stretching
1048.62	1066.83	C-O stretching of carbonyl

A broad and strong band at 3419 cm⁻¹ was characteristic for O-H and N-H groups. The band at 2923 cm⁻¹ was ascribed to the asymmetric stretch of CH₂ groups. The peak at 1646 cm⁻¹ was attributed to C=O stretching vibration. The peak at 1048 cm⁻¹ assigned to stretching of alcoholic C-O groups on the biomass surface.

After copper(II) adsorption, OH stretching vibration was shifted to 3416 cm⁻¹. The obvious shift to the lower wavenumber after adsorption suggested that chemical interactions between the metal ions and the OH groups occurred on the biomass surface. The C=O peak was observed at 1649 cm⁻¹. In addition, the peak of C-O groups shifted to 1067 cm⁻¹. These results indicated that the O-H, C=O, C-O and =NH functional groups play a major role in binding copper(II).

Effect of pH: The pH dependence of metal adsorption is largely related to the surface functional group in the adsorbent and metal solution chemistry¹⁰. Fig. 1 shows the effect of pH on copper(II) removal. The results indicated that the adsorption quantity increased from 30.73–43.70 mg g⁻¹ as the pH value ranged from 2.8–4.4. Similar observations have been earlier recorded. This was because the point of zero charge (pH_{ZPC}) for *F. camelliae* was *ca.* 3.3. Polar functional groups, acrylamide, amino and carboxyl were protonated at lower pH and the electrostatic force of repulsion was inimical to the adsorption. In the pH range of 2.8–4.4, adsorbent surfaces were more negatively charged and the repelling forces diminished when the pH values increased.

Fig. 1. Effect of pH on the adsorption of copper(II) onto *F. camelliae*

Chemical species are also possible mechanism affecting the adsorption. In this study, maximum adsorption is observed at pH 5.5, which might be partly due to the hydrolysis of copper(II), leading to the formation of copper(II)-OH⁺. Larger radii and less positive charge made the acting force between the complexes of copper(II) and negative charged adsorbent weakened. Hence, the retention would slowdown.

Effects of contact time and temperature: Fig. 2 indicates the effect of contact time on the adsorption process. It can be seen that the adsorption capacity rapidly increased in the first 0.5 h after which adsorption capacity gradually approached equilibrium. In general, *ca.* 96.5 % of the total copper(II) was removed within 1 h. Therefore 1 h was deemed suitable to establish equilibrium in subsequent experiments.

Fig. 2. Effect of contact time on copper(II) adsorption at various temperatures

Fig. 2 also showed that higher temperature favored the adsorption process, indicating the endothermic nature of copper(II) adsorption onto *F. camelliae* biomass.

Adsorption isotherm: The equilibrium concentration dependence data (Fig. 3) was tested using different adsorption isotherm models in order to develop an equation which can accurately represent the results and can be used for design purpose. Several isothermal equations are available for analysis. In this study, Freundlich, Langmuir and Dubinin-Radushkevich (D-R) models were employed.

Fig. 3. Plot of q_e versus C_e at different temperatures

Freundlich model: The empirical equation of Freundlich can be applied for non-ideal adsorption on heterogeneous surfaces and multilayer adsorption¹¹. This model can be written as:

$$q_e = K_f C_e^{1/n} \quad (1)$$

where K_f [(mg g^{-1})/(mg L^{-1})^{1/n}] and n (dimensionless) are capacity constant and empirical parameter relating to the affinity, respectively.

Parameters of the model were shown in Table-2. The results indicated that the Freundlich model can not adequately describe the isothermal adsorption process since the correlation coefficients were found to be only 0.90-0.97 and the $1/n$ values were ruleless.

Langmuir model: The Langmuir model assumes that adsorption occurs at specific homogeneous sites on the adsorbent and was used successfully in many monolayer adsorption processes. This model can be expressed as follows¹⁰.

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2)$$

where q_m (mg g^{-1}) is the maximum amount of copper(II) adsorbed on the biomass and b (L mg^{-1}) is a constant related to the affinity of the binding sites. q_e (mg g^{-1}) is the adsorption capacity at equilibrium.

The Langmuir plots for copper(II) isothermal adsorption process were shown in Fig. 4 and the adsorption constants were given in Table-2. The data fitted well in the Langmuir equation, as shown by the regression coefficient values R in the entire concentration range studied. The values of q_m and b increased with the rise of temperatures, indicating an endothermic adsorption process in nature.

Dubinin-Radushkevich (D-R) model: In order to distinguish the adsorption mechanism, the Dubinin-Radushkevich

Fig. 4. Linear plots of Langmuir isotherm at different temperatures

model was also analyzed in this study. The D-R equation has the linear form⁷ as follows:

$$\ln q_e = \ln q_D - \beta \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \quad (3)$$

where q_D is theoretical saturation capacity, which can represent the total specific micropore volume of the adsorbent. β ($\text{mol}^2 \text{kJ}^{-2}$) is related to the mean free energy (E , kJ mol^{-1}) of adsorption per mole of the adsorbate and can be calculated using the relationship⁷:

$$E = \frac{1}{\sqrt{2\beta}} \quad (4)$$

The parameters of D-R equation are listed in Table-2. The E values in this study were found to be higher than 11 kJ mol^{-1} at all studied temperatures, indicating a chemical ion-exchange process according to the literature.

Thermodynamics of adsorption: The thermodynamic parameters (ΔG° , ΔH° and ΔS°) were determined by using the following equations:

$$\ln b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

where b is Langmuir constant. According to eqn. 6, the ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot of $\ln b$ versus $1/T$ yields, respectively. All the results are recorded in Table-3.

The negative ΔG° values indicated thermodynamically feasible and spontaneous nature of the adsorption. ΔG° values varied from -21.99 to $-28.02 \text{ kJ mol}^{-1}$ in the range of 285-318 K. The results implied that the adsorption of copper(II) onto

TABLE-2
ISOTHERM PARAMETERS FOR THE ADSORPTION OF COPPER(II) ON THE BIOMASS

Temperature (K)	Freundlich isotherm			Langmuir isotherm			D-R isotherm		
	$1/n$	K_f (mg g^{-1})	R	b (L mg^{-1})	q_m (mg g^{-1})	R	q_m (mmol g^{-1})	E (kJ mol^{-1})	R
285	8.42	0.3712	0.9195	0.1019	56.38	0.9998	0.75	11.6102	0.9472
295	9.95	0.3501	0.9355	0.1100	61.28	0.9997	0.74	12.4608	0.9687
305	9.18	0.3786	0.9201	0.0862	69.35	0.9994	0.95	12.1258	0.9511
318	18.32	0.2778	0.9781	0.3185	75.20	0.9999	0.72	15.3214	0.9899

TABLE-3
THERMODYNAMIC PARAMETERS FOR THE
ADSORPTION OF COPPER(II) ON THE BIOMASS

Temp. (K)	b (L mg ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
285	0.10188	-21.99	23.02	161.3
295	0.11032	-23.87		
305	0.08689	-25.19		
318	0.3250	-28.02		

F. camelliae was enhanced by high temperature. The positive ΔH° (23.02 kJ mol⁻¹) further confirmed the endothermic nature of the adsorption process. The positive ΔS° (161.3 J mol⁻¹ K⁻¹) was characteristic of increased randomness at the solid-solution interface during the adsorption process¹. In the adsorption of copper(II), the adsorbate species displaced adsorbed solvent molecules to gain more translational entropy than was lost by the adsorbate ions, thus allowing randomness in the system¹².

Desorption experiments: Desorption studies were carried out to understand the bonding strength of copper(II) with *F. camelliae*. Deionized water (DW), HCl solution (0.5 mmol L⁻¹) and NaCl solution (0.5 mmol L⁻¹) were used as eluent. Results were shown in Fig. 5 which indicated that Pb(II) ions were chemically fixed on the *F. camelliae* other than physical adsorption by electrostatic attraction. For reuse purpose, the adsorbent can be regenerated in acid media.

Fig. 5. Effect of eluent type on the desorption percentage

Recovery experiments: In order to reclaim copper(II) from the environment to eliminate pollution completely, the copper(II)-loaded-*F. camelliae* was incinerated to ash. Nitric acid solution (2 % w/v) was added to the ash to dissolve the residue. The solution was then diluted to 50 mL and assayed

with AAS for copper(II) concentration. The average recovery percentage amounted to 96.20 %. This result suggested that the removal and reclamation of Pb(II) from aqueous solution with *F. camelliae* was practical and efficient.

Implication for the tea plant: Based on the above analysis, conclusions can be drawn that *F. camelliae* is an effective adsorbent for the removal of copper(II). It has positive significance in terms of environmental pollution control. However, tea leaves combine with lead readily especially in weak acid conditions, which went against the producing of pollution-free food. Hence, tea garden must be kept away from high way and industrial park. The polluted water should be absolute prohibitions in tea garden irrigation.

Conclusion

Waste *F. camelliae* is an idea adsorbent for the removal of lead ions from aqueous solutions. Equilibrium data were best described by the Langmuir model. The highest monolayer adsorption capacity was 75.20 mg g⁻¹. The lead adsorption was spontaneous and endothermic in nature and the adsorption process may mainly be chemical ion-exchange mechanism. Acylamide, carbonyl, amino, carboxyl and hydroxyl groups were responsible for the adsorption behavior. copper(II) fixed on *F. camelliae* can be reclaimed by incineration. It is a sound technique considering the high efficiency, low cost and pollution. On the other hand, it is worthy of being alert about the environment of tea planting garden to prevent the health threat from lead pollution.

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