

Agar-encapsulated adsorbent based on leaf of platanus sp. to adsorb cadmium ion in water

Eko Siswoyo, Nozomi Endo, Yoshihiro Mihara and Shunitz Tanaka

ABSTRACT

A low cost and environmentally friendly adsorbent was developed based on leaf of platanus sp. to adsorb cadmium ion in water. The adsorbent was modified with citric acid and then also encapsulated in agar for easy separation after the adsorption process. Parameters such as adsorbent dose, stirring time, solution pH and modification of the adsorbent with citric acid were investigated in a batch experiment in order to determine the optimum condition for Cd (II) adsorption. Based on the Langmuir isotherm adsorption model, the adsorption capacity of cadmium ion for raw adsorbent, modified adsorbent with citric acid and encapsulated adsorbent were 3.69, 15.31 and 6.89 mg/g, respectively. The high adsorption capacity after treatment with citric acid may be due to the increase in carboxylic content of the adsorbent surface and also the increase of surface area and pore volume of the adsorbent. With this high adsorption capacity for cadmium ion and an abundance of raw materials, this bio-adsorbent could be considered as a low cost adsorbent in the near future.

Key words | cadmium ion, citric acid, encapsulated adsorbent, low cost adsorbent, platanus leaf

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INTRODUCTION

The issue of environmental contaminations with heavy metals is considered a serious environmental problem because of its potential for damage to human health and the environment. In the environment, the presence of cadmium, one of the most toxic metal ions, sometimes leads to a serious problem for human beings and the ecosystem. Cadmium can be released to the environment through many industrial activities such as ceramics, metal plating, textiles, etc. (Rao *et al.* 2006; Wang *et al.* 2009). Itai-itai disease was caused by cadmium poisoning, which resulted in softening of the bone and kidney failure in the Jinzu River area of the Toyama Prefecture, was one of the most severe environmental events in Japan. The rate of death among patients was 72.6% and it is considered that itai-itai disease has a long-lasting negative effect on a patient's life span (Kawano *et al.* 1986).

Many technologies have been employed in order to minimize the pollution problem of heavy metals; for example, membrane technology, ion exchange, phytoremediation, adsorption, etc. Adsorption is one of the common methods that have been widely used for water and wastewater treatment. As an adsorbent, activated carbon has often been utilized in many countries; however, this material is quite expensive. The high cost of activated

carbon has inspired many studies into the development of alternative low cost adsorbent materials.

Recently, some researchers have been attracted to the development of bio-adsorbents based on the leaves of some plants due to the high removal capacity for adsorbing heavy metal ions from solution. For example, *Pinus roxburghii* leaves were utilized to remove heavy metals from industrial effluent (Tewari & Vivekanand 2013). In order to increase the adsorption capacity, bio-adsorbents were modified with some chemicals. Li *et al.* (2013) reported that modification of *Imperata cylindrical* leaf powder using sulphuric acid and phosphoric acid resulted in high adsorption capacity for nickel in solution. Chemical modification on *Moringa oleifera* leaf powder using NaOH followed by citric acid was applied for the adsorption of Cd (II), Cu (II) and Ni (II) (Reddy *et al.* 2012).

In Japan and many other northern hemisphere countries, the platanus tree is abundant and often used as ornamental and roadsides trees. The fallen leaves of this tree are usually collected and disposed of as garbage in Japan. The leaf of this tree has potential as a low cost and environmentally friendly adsorbent material; however, the study of the utilization of the leaf of the platanus tree as an adsorbent material is still limited.

The purpose of this study was to investigate the adsorption capacity of an adsorbent encapsulated in agar based on the leaf of platanus sp. for the removal of cadmium ion in water. Powdered platanus leaf was treated with citric acid and then encapsulated in agar as a binder material for easy separation of the adsorbent from solution after the process of adsorption of cadmium ion.

MATERIALS AND METHODS

Preparation of adsorbent and stock solution

Adsorbents were prepared based on leaf of platanus sp. collected from the Hokkaido University campus area. The dry leaf was rinsed with tap water, then washed continuously with distilled water to remove dirt and other particulate matter, dried at 80 °C for 24 hours and then crushed into powder form. In order to increase the adsorption capacity of the adsorbent, 1.3 M of citric acid was utilized as an activator agent with a composition of 1 g (adsorbent): 4 mL (citric acid) and then heated at 150 °C for 30 min. The activated adsorbent then was encapsulated in agar with the ratio of 1 g (agar): 2.5 g (activated adsorbent).

The stock solution of cadmium ion (Cd^{2+}) was prepared with $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ from WAKO Pure Chemical Co. (Osaka, Japan). The standard solutions for analysis of Cd^{2+} by atomic adsorption spectrophotometer (AAS HITACHI A-2000, Hitachi, Japan) were prepared by using a pure standards solution from WAKO Pure Chemical Co. (Osaka, Japan).

Characterization of adsorbent

In order to obtain the surface area of the adsorbent, scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) (JEOL JSM-6360 LA, Japan) was employed. Furthermore, the elemental test was undertaken using an elemental instrument (MICRO CORDER JM10, Yanaco, Japan) in order to determine the amounts of C, H, N, O, S and ash of the adsorbent material. Fourier transform infrared spectroscopy (FTIR) (FT/IR-4100) and Brunauer-Emmett-Teller (BET) (BELSORP-mini, BEL Japan Inc., Osaka, Japan) were utilized in order to determine the functional groups, surface area and pore volume of adsorbent materials.

Adsorption experiment

The adsorption process in the present study was conducted using a batch system. Parameters such as mass of adsorbent,

pH of the solution, stirring time and initial concentration of cadmium ion in the solution were investigated in order to determine the ability and the optimum condition for adsorption using this adsorbent. In order to estimate the effect of the mass of the adsorbent, 25–200 mg of adsorbent was added to 50 ml of cadmium solution and agitated at 1,000 rpm for 2 hours using a shaker (EYELA Cute Mixer CM-1000). The influence of pH on the adsorption of cadmium ion was investigated by using a solution of pH 2 to 8. Acetic buffers, HNO_3 and NaOH were utilized to adjust the desired pH of the solution. Various stirring times from 15 to 1,440 min were applied in order to determine the influence of stirring time on the adsorption of cadmium ion. After reaching equilibrium, the solution was centrifuged at 4,000 rpm for 5 min using a centrifuge (IEC61010-2-020, KUBOTA, Japan) and then the concentration of cadmium ion in the supernatant solution was determined using a flame atomic absorption spectrophotometer (HITACHI A-2000, Japan).

RESULTS AND DISCUSSION

Properties of adsorbent

Table 1 shows the composition of C, H, O, N, S and ash of adsorbent materials before and after being activated with citric acid. The amount of O in the adsorbent material significantly increased from 23.03 to 40.22% and ash decreased from 20.11 to 1.79% after treatment with citric acid.

The SEM photograph of adsorbent materials before and after being activated with citric acid are shown in Figure 1. It can be seen that the surface of the adsorbent after modification with citric acid appears to be more porous compared to raw adsorbent. Treatment of the adsorbent material with citric acid resulted in more pores on the surface of the adsorbent.

Table 1 | Elemental analysis of adsorbent materials before and after treatment with citric acid

Element (%w/w)	Adsorbent	
	Raw adsorbent	After treatment with citric acid
Carbon (C)	49.90	49.90
Hydrogen (H)	5.78	6.14
Oxygen (O)	23.03	40.22
Nitrogen (N)	1.10	1.95
Sulphate (S)	0	0
Ash	20.11	1.79

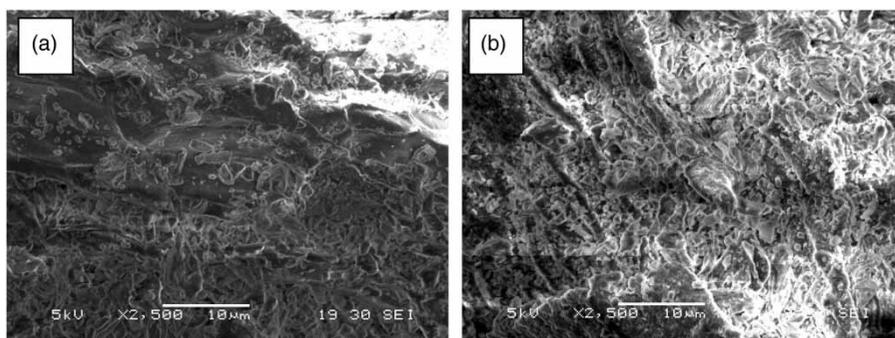


Figure 1 | SEM photograph of adsorbent. (a) Raw adsorbent. (b) After being activated with citric acid.

Based on the data obtained by BET analysis, the surface area and volume of adsorbent pores before and after modification with citric acid are $19.28 \text{ m}^2 \text{ g}^{-1}$ and $4.43 \text{ cm}^3 \text{ g}^{-1}$, and $31.81 \text{ m}^2 \text{ g}^{-1}$ and $7.31 \text{ cm}^3 \text{ g}^{-1}$, respectively. These data support the SEM photograph in that modification with citric acid resulted in more pores on the surface of the adsorbent.

FTIR analysis was employed in order to identify the characteristic functional groups on the surface of adsorbents. Figure 2 shows the FTIR spectra of the adsorbents before and after being activated with citric acid. The FTIR spectrum of raw adsorbent and activated adsorbent showed a broad peak at $3,400 \text{ cm}^{-1}$, indicating the presence of macromolecular compounds such as cellulose, lignin, pectin, etc. The double peaks that appeared in both spectra at wave numbers $2,922$ and $2,849 \text{ cm}^{-1}$ may be due to the asymmetric and symmetric stretch of aliphatic chains (-CH), respectively. The peak around

$1,435\text{--}1,251 \text{ cm}^{-1}$ indicated the characteristic main skeleton of cellulose (Reddy *et al.* 2012). The peak around $3,371 \text{ cm}^{-1}$ indicated the presence of carboxylic O-H groups, and the peaks around $1,067 \text{ cm}^{-1}$ indicated C=O group of primary hydroxyl stretching, which may be attributed to the cellulose structure of platanus (Nguyen & Ha 2009). The activated adsorbent has a strong characteristic stretching vibration absorption band of carboxyl group at $1,719 \text{ cm}^{-1}$ as an effect of treatment with citric acid.

Based on the data obtained by SEM, FTIR and BET analysis, it can be concluded that modification with citric acid resulted in physical and chemical properties on the surface of the adsorbent and increased the adsorption capacity of cadmium in water. The increase of the sorption of metal ions may be due to the esterification process, which also increases the carboxylic content of the surface of the adsorbents (Low *et al.* 2004).

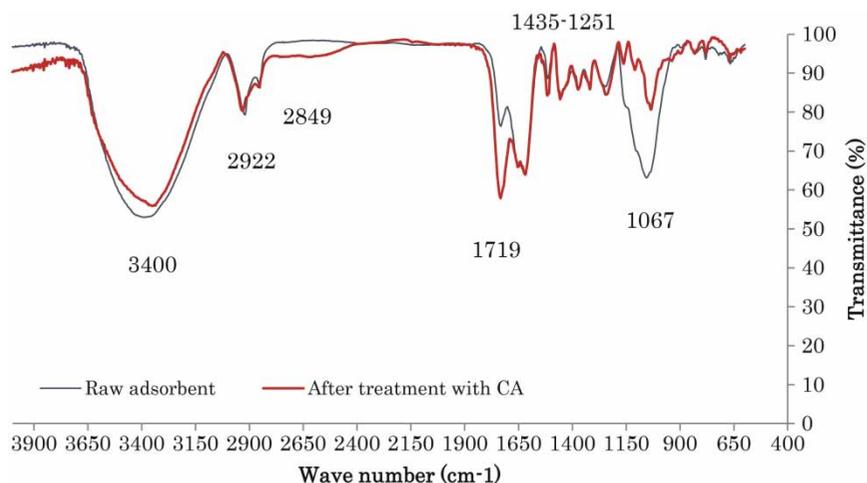


Figure 2 | FTIR spectra of adsorbent before and after treatment with citric acid.

Effect of dose of adsorbent on the adsorption of cadmium ion

The effect adsorbent dose is shown in Figure 3. For 10 mg/L of initial cadmium concentration, the adsorption capacity for all mass of adsorbent from 25 to 200 mg was almost constant; therefore, 25 mg was favorable as an ideal mass for adsorbent. When the initial concentration of cadmium increased, the removal efficiency of adsorption increased linearly by the increase of adsorbent mass and became constant from 150 mg. This result proved that the adsorption of cadmium ion in water was absolutely due to the presence of the adsorbent.

Effect of pH

The binding of cadmium ion (Cd^{2+}) with the surface functional groups of adsorbent strongly depended on the solution pH. Figure 4 shows the effect of pH on the adsorption of cadmium ion in water. The removal efficiency of cadmium ion increased with the increase of pH because cadmium ion forms a complex with some acidic functional groups in the adsorbent (Khalifa & Bagane 2011). The removal of metal cation at any pH was much greater than that by hydroxide precipitation. Adsorption of metal cation on adsorbent was influenced by the nature of the adsorbent surface and the distribution of metal species, which also depends on the pH of the solution. The removal efficiency of cadmium decreased with the decrease of pH because protons compete with metal ion for the binding sites on the adsorbent surface. Furthermore, the protons decrease negative charges by association of the functional group with protons (Siswoyo & Tanaka 2013). The increase in the removal of metal ions as pH increases can be explained on the basis of the decrease in H^+ on the surface, which results in less repulsion than with metal ions (Namasivayam & Ranganathan 1995; Kadirvelu & Namasivayam 2005;

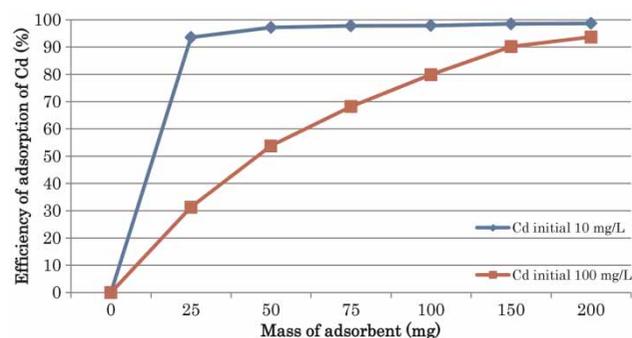


Figure 3 | Effect of dose of adsorbent on cadmium adsorption (volume of Cd soln.: 50 ml, Cd initial.: 10 mg/L, pH of soln.: 6, and stirring time: 2 hours).

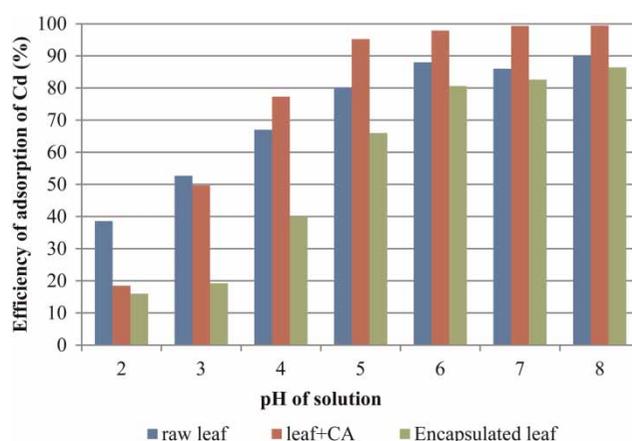


Figure 4 | The influence of pH on the adsorption of cadmium (mass of adsorbent: 100 mg, volume of Cd soln.: 50 ml, Cd initial.: 10 mg/L, and stirring time: 2 hours).

Souag *et al.* 2009). In the highly acidic medium, the dissolution of the adsorbent appears to consequently decrease in the active sites of the adsorbent. The highly protonated adsorbent surface is not favorable for the uptake of cadmium ion because of electrostatic repulsion (Singh *et al.* 1998; Papandreou *et al.* 2007).

It is known that the precipitation of cadmium ion in solution starts at around pH 8.5 (Lee & Davis 2001; Wang *et al.* 2009; Khosravan & Lashkari 2011). The recent study confirmed that cadmium ions were precipitated at pH 9, and pH 6 to 8 was ideal for adsorption of cadmium ion using this adsorbent.

Effect of stirring time

The effect of stirring time on the adsorption of cadmium ion is shown in Figure 5. The equilibrium adsorption for powder and encapsulated adsorbent on 10 mg/l of cadmium was achieved after around 30 and 1,440 min, respectively. The equilibrium time of the encapsulated adsorbent was longer than the powder adsorbent because the binding site of the encapsulated adsorbent is covered by agar, and the quick equilibrium time is due to the particle size (Messaouda *et al.* 2012). This result is important because the equilibrium time is one of the considerations for economical application in wastewater treatment plants (Kadirvelu & Namasivayam 2003; Rao *et al.* 2006).

Adsorption isotherm

The Langmuir and Freundlich isotherm models were applied to the equilibrium constant of adsorption by the following equations.

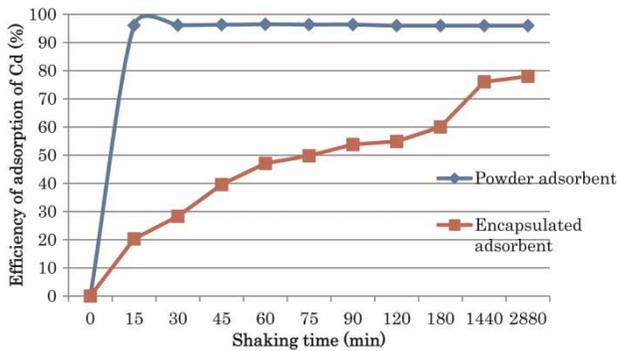


Figure 5 | The influence of stirring time on the adsorption of cadmium (mass of adsorbent: 100 mg volume of Cd soln.: 50 ml, pH of soln.: 6.0, and Cd initial: 10 mg/L).

The equation of the Langmuir isotherm model

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L \cdot q_m} \tag{1}$$

where C_e is the equilibrium concentration (mg/l), q_e is the adsorbed amount of cadmium at equilibrium (mg/g), q_m and K_L are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. From the equation above, a plot of C_e/q_e versus C_e will be used to determine the values of q_m and K_L as the tangent and intercept of the curve.

The equation of the Freundlich isotherm model

$$q_e = K_f C_e^{1/n} \tag{2}$$

where q_e is the amount of adsorbed (mg/g), C_e is the equilibrium concentration (mg/l) and K_f and n are constants. To determine the amount of K_f and n , plots between $\log C_e$ and $\log q_e$

$$\text{Log}(q_e) = \text{log}(K_f) + 1/n \text{log}(C_e) \tag{3}$$

The Langmuir adsorption isotherm is shown in Figure 6 and the result of the Langmuir and Freundlich isotherm

Table 2 | The result of Langmuir and Freundlich isotherm models

Adsorbent	Langmuir model			Freundlich model		
	qm (mg/g)	K_L (l/mg)	R^2	K_f	n	R^2
Inactivated	3.69	6.29	0.978	4.403	2.61	0.972
Activated with citric acid	15.31	1.36	0.939	6.725	3.27	0.993
Encapsulated in agar	6.89	2.48	0.948	4.709	2.64	0.991

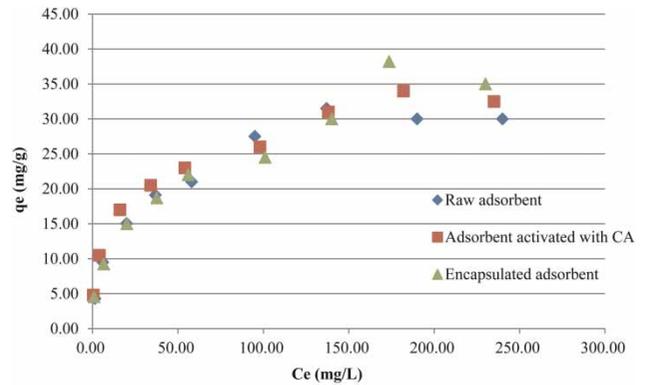


Figure 6 | Langmuir isotherm for adsorption of Cd(II) (mass of adsorbent: 100 mg, volume of Cd soln.: 50 ml, pH of soln.: 6.0, and stirring time: 2 hours and 24 hours for encapsulated adsorbent).

models of inactivated, activated and encapsulated adsorbents determined from the above equations are shown in Table 2.

The essential characteristics of the Langmuir isotherm can be expressed due to a dimensionless constant of the separation factor or equilibrium parameter, R_L , which is defined as

$$R_L = 1/(1 + K_L C_0) \tag{4}$$

where K_L is the Langmuir constant and C_0 is the initial concentration of cadmium ion in the solution. The R_L value indicates the shape of the isotherm as follows:

$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The R_L value between 0 and 1 is favorable adsorption (McKay *et al.* 1982). The R_L values of raw, modified and encapsulated adsorbents for the concentrations of 10 mg/L Cd^{2+} were 0.016, 0.069 and 0.039, respectively. It means that the bio-adsorbents based on platanus leaf were favorable for the adsorption of cadmium ion in water.

CONCLUSION

The present study shows that bio-adsorbents based on platanus leaf modified with citric acid achieve high efficiency on

the adsorption of cadmium ion in water. The batch adsorption experiments have been conducted in different initial cadmium ion concentration, dose of adsorbent, contact time and solution pH. The adsorption of cadmium ion was strongly pH-dependent and pH 6 to 8 was favorable for the adsorbent. Encapsulation of the bio-adsorbent in agar decreased the adsorption capacity of cadmium ion; however, the adsorbent material can be separated easily after the adsorption process. Finally, with this high efficiency, easy-to-separate, low cost and environmentally friendly process for the removal of cadmium ion in water, the adsorbents could be considered as a promising solution for water and waste water treatment in the near future.

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