BIOSORPTION BEHAVIOR OF CD(II) IONS ONTO TAPIOCA PEEL: EQUILIBRIUM, KINETICS, THERMODYNAMICS AND DESORPTION STUDIES

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Abstract

The biosorption behavior of Cd(II) from aqueous solution onto industrial waste such as tapioca peel was investigated as a function of influence parameters such as contact time, solution pH, initial concentration, temperature, desorption, and regeneration. Results showed that the biosorption was relatively fast, and equilibrium was achieved within 30 min. The tapioca peel exhibited good biosorption potential at pH 5. The experiment data was described better by the Langmuir than the Freundlich isotherm model, with a maximum biosorption capacity of 36.10 mg/g. The biosorption kinetics followed a pseudo-second-order model, and the thermodynamic behaviour indicated that the Cd(II) biosorption onto tapioca peel was an endothermic process. The results of FTIR spectroscopic analysis revealed that hydroxyl and carboxyl groups on the tapioca peel surface were involved in the biosorption of Cd(II). Desorption of Cd-loaded tapioca peel was desorbed by HCl, HNO_3, H_2SO_4, EDTA, $MgCl_2$, and NaCl as the desorbing agents. The results showed that more than 86% desorption of Cd(II) was attained with 0.1 M HCl. The regeneration experiments showed that the biosorption

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capacity of tapioca peel was a total slightly reduced 6%. Meanwhile, the recovery of Cd(II) was decreased from 88.74 to 70.91% in the sixth cycle.

Keywords: Biosorption, Desorption, Tapioca peel, Biosorbent, Cd(II)

Introduction

Water pollution by heavy metals has been an important ecological and environmental issue in Thailand. Cd(II) is one of the heavy metals that is regarded as an element of high toxicity. Cd(II) toxicity can lead to cancer, hypertension, renal dysfunction, hepatic injury, and lung insufficiency (Sari et al., 2008). Industrial effluents from electroplating, pigments, battery, solar cells, plastic stabilizers, mining, metallurgical, and fertilizer industries are the major sources of Cd(II) contaminants in water resources (Gupta et al., 2022). Conventional methods for the removal of Cd(II) from wastewater are ion exchange, ultrafiltration, adsorption, solvent extraction, chemical precipitation, reverse osmosis, and phytoremediation (Wattanakornsiri et al., 2022). However, the disadvantages of the methods include being extremely expensive and not effective, especially when the metal concentration is less than 100 mg/L (Volesky, 2007)

Biosorption is one alternative that should be considered; the advantages of this method over conventional methods include great efficiency for metal removal at low concentration, the possibility of metal recovery, and the low cost of biosorbent. Researchers have tested many materials such as rice husk, tea waste, coffee bean, coconut waste, peanut shell, sunflower stalk, orange peel, banana peel, mango peel, pomelo peel, sugarcane bagasse and melon peel for Cd(II) removal from wastewater (Kwikima et al., 2021; Ahmadi et al., 2022).

Tapioca is an annual tuber crop grown widely in tropical areas. Currently, Thailand is also the world's largest exporter of tapioca products with an average of 7 million tons/year. However, the tapioca industry produces large quantities of wastes and creates environmental problems. Finding a use for large quantities of tapioca peel is one of the challenge tasks. The objective of the present work was to explore the potential of tapioca peel for the biosorption of Cd(II) from aqueous solution. The influence of various experimental parameters such as contact time, solution pH, initial concentration, temperature, desorption, and regeneration have been investigated. FTIR analysis, biosorption isotherms, kinetics, and thermodynamic model were used to evaluate the experimental data and to describe the possible biosorption mechanism.

Materials and methods

Biosorbent preparation

Tapioca peel was generated in the native tapioca starch production process from the J.Charoen Marketing Co., Ltd., in Chiangkan district, Loei Province, Thailand. The peels were washed 4-5 times with distilled water and dried in an oven at 80 °C for 48 hours, and then crushed and sieved through different sizes. 0.425-2.36 mm fraction was used in all experiments.

Fourier transform infrared analysis

The functional groups present on the surface of tapioca peel before and after Cd(II) biosorption were analyzed by FTIR spectroscopy (Bruker, Tensor 27). The analysis was carried out using KBr, and the spectra range varied from 4000 to 400 cm^{-1}.

Metal solutions

All chemicals used in the present work were analytical grade and were purchased from Loba Chemie (Mumbai, India). The stock solution of Cd(II) was prepared by dissolving the required amount of $Cd(NO_3)_2 \cdot 4H_2O$ in distilled water. The pH of solutions was adjusted by pH meter (Mettler-Toledo, S20) using 0.1 M HNO_3 and 0.1 M NaOH.

Biosorption studies

The Cd(II) biosorption experiments to examine the effects of the parameters such as contact time, solution pH, initial concentration, and temperature were carried out in 250 mL Erlenmeyer flasks containing 100 mL metal solutions and 1 g of tapioca peel. The flasks were agitated at 200 rpm in the orbital shaker (Forma Scientific, model 420) at a temperature of 35°C. Tapioca peel was separated using fiberglass filter paper, and the Cd(II) concentration in solution was analyzed by AAS (Shimadzu, AA-6200) and operated at an analytical wavelength of 228.8 nm. The effect of contact time was studied at definite time intervals (5, 10, 20, 30, 60, 90, and 120 min). The effect of pH was determined in different pH solutions (2, 3, 4, 5, 6, and 7). The effect of initial concentration was varied over a range concentration (25, 50, 100, 200, 300, 400, and 500 mg/L), and the effect of temperature was incubated at different degrees (5, 15, and 55°C). All experiments were carried out in triplicate, and the results were presented as mean values. The amount of Cd (II) biosorption at equilibrium, q_e (mg/g), was calculated as follows:

$$q_e = \frac{V}{M}(C_0 - C_e) \tag{1}$$

Where: C_0 and C_e are the initial and equilibrium concentrations of Cd(II) in solution (mg/L). V and M are the volume of solution (L) and mass of tapioca peel (g).

Desorption and regeneration studies

Desorption experiments were carried out by treating 1 g of tapioca peel with 100 mL of 50 mg/L Cd(II) solution. After Cd(II) biosorption, the Cd-loaded tapioca peel was filtered, washed several times with distilled water to remove residual Cd(II), and desorbed with 100 mL of 0.1 M HCl, HNO_3, H_2SO_4, EDTA, $MgCl_2$, and NaCl. The mixtures were shaken in the orbital shaker for 30 minutes, and the filtrates were analyzed to determine the concentration of Cd(II) after desorption. The desorbed peel was washed, and the so regenerated biosorbent was used in six biosorption–desorption cycles to determine reusability of the peel. Desorption efficiency was calculated as follows:

$$\text{Desorption efficiency } = \frac{\text{Amount of Cd(II) desorbed}}{\text{Amount of Cd(II) adsorbed}} \text{ X } 100 \qquad (2)$$

Results and discussion

Effect of contact time

Contact time is one of the important parameters that attributed to the success of the biosorbents in metals biosorption. The results showed that the biosorption of Cd(II) increased as the contact time was increased, and the figure showed two phases of rapid and slow rates (Fig.1). The biosorption capacity of Cd(II) increased rapidly during the first 5 minutes. After that, the capacity increased slowly until the equilibrium was reached at 30 minutes, when biosorption equilibrium was found to be 4.27 mg/g. The rapid phase is attributed to the highly porous structure and the large surface area of the tapioca peel, which provides ready access for the removal of Cd(II) on the active sites. With the gradual occupancy of these sites, the process becomes less efficient in the slower phase. Similar observations of two-rate biosorption were reported for the removal of Cd(II) by mungbean husk (Saeed et al., 2009), physic seed hull (Mohammad et al., 2010) and leaves waste (Gupta et al., 2022).

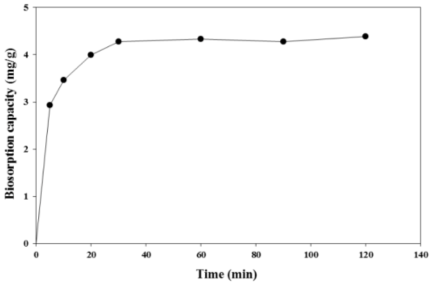

Fig. 1 Effect of contact time on the biosorption of Cd(II) onto tapioca peel

Effect of solution pH

It is well known that solution pH is one of the major parameters controlling the biosorption of metals ions with biosorbents. The results showed that the biosorption capacity was increased with increasing solution pH (Fig.2). This can be explained by the fact that at low pH, the surface of the tapioca peel would also be surrounded by H^+, which decreases the Cd(II) interaction with the active sites of the tapioca peel by greater repulsive force, while with an increase in pH, the total surface of the tapioca peel became negative; therefore, biosorption increased (Benaissa & Elouchdi, 2007; Ahmadi et al., 2022) and the maximum biosorption occurred at pH 5, when the capacity was found to be 4.29 mg/g. However, the decrease in biosorption efficiency at higher pH (>5) was due to the formation of soluble hydroxylated complexes and their competition with the active sites as a result, the retention would decrease again (Kumar et al., 2011).

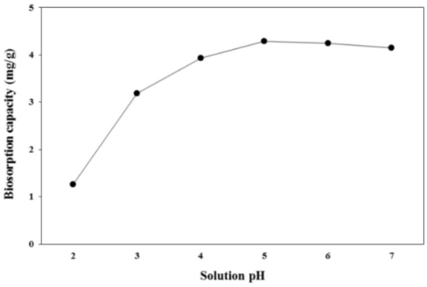

Fig. 2 Effect of pH on the biosorption of Cd(II) onto tapioca peel

Biosorption isotherms

The biosorption isotherm is the relationship graph between the amounts of Cd(II) adsorbed onto the surface of tapioca peel at equilibrium (Fig.3). The results showed that the biosorption capacity increased with an increased concentration. When the initial concentration increased from 25 to 500 mg/l, the biosorption capacity increased from 2.36 to 31.87 mg/g. The biosorption isotherms were studied using two models, namely the Langmuir and Freundlich isotherm. The Langmuir model assumes adsorption on a homogeneous surface and a monolayer adsorption, and the equation is expressed as follows:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{3}$$

Where: q_{max} and K_L are the maximum capacity (mg/g) and Langmuir constant (L/mg). The values of q_{max} and K_L can be calculated from the slope and intercept of the plot between C_e/q_e versus C_e.

The Freundlich isotherm assumes adsorption on a heterogeneous surface and a multilayer adsorption and the equation is expressed as follows:

$$q_e = K_F C_e^{1/n} \tag{4}$$

Where: K_F and $1/n$ are the biosorption capacity and biosorption intensity. The values of K_F and $1/n$ can be calculated from the slope and intercept of the plot between log q_e versus log C_e.

The results showed that (Fig. 4 and 5) the biosorption isotherm for the tapioca peel was described well by the Langmuir model (R^2=0.9889) as compared to the Freundlich model (R^2=0.9492). In other words, the biosorption process took place through a monolayer coverage of Cd(II) ions on the surface of tapioca peel, and the maximum capacity (q_{max}) obtained in this study was 36.10 mg/g (Table 1). Moreover, the maximum biosorption capacity of tapioca peel in this work is higher than that of various biosorbents reported in the literature (Table 2).

Table 1 Isotherm parameters obtained from Langmuir and Freundlich model

Langmuir isotherm			Freundlich isotherm		
q_{max}	K_L	R^2	K_F	1/n	R^2
36.10	0.0353	0.9889	2.21	0.553	0.9492

Table 2 Comparison of cadmium biosorption capacities of various biosorbents

Biosorbents	Capacity (mg/g)	Reference
Banana peel	2.18	(Anwar et al., 2010)
Physic seed hull	11.89	(Mohammad et al., 2010)
Corn stalk	12.73	(Zheng et al., 2010)
Wheat straw	14.80	(Dang et al., 2009)
Coffee grounds	15.65	(Azouaou et al., 2010)
Pomelo peel	21.83	(Saikaew et al., 2009)
Mungbean husk	35.41	(Saeed et al., 2009)
Tapioca peel	**36.10**	**This work**

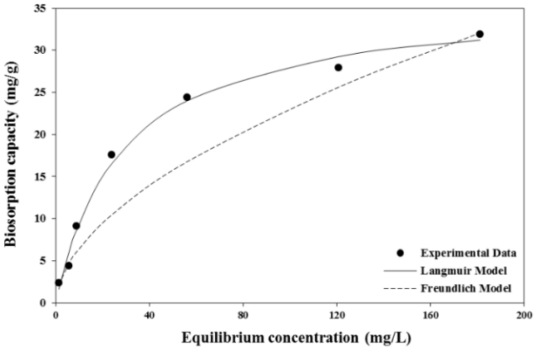

Figure 3 Biosorption isotherms of Cd(II) onto tapioca peel

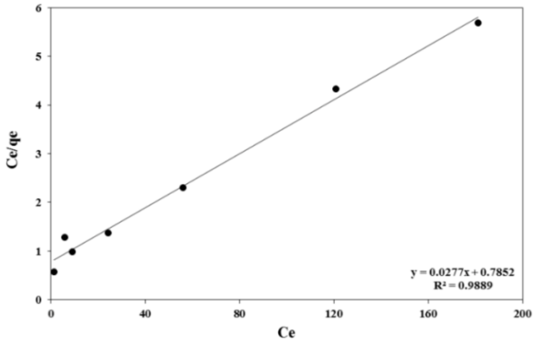

Figure 4 Langmuir isotherm plots of Cd(II) onto tapioca peel

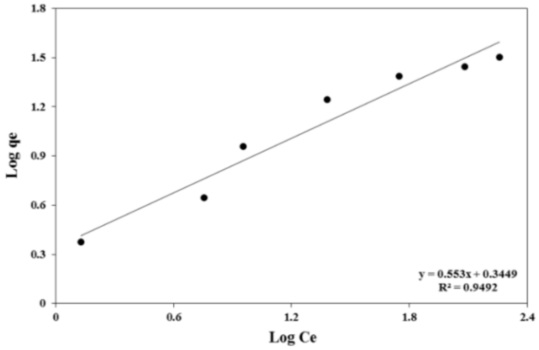

Figure 5 Freundlich isotherm plots of Cd(II) onto tapioca peel

Biosorption kinetics

To describe the possible biosorption mechanism of Cd(II) onto tapioca peel and rate the controlling steps, the kinetic models were studied using two models, namely pseudo-first-order and pseudo-second-order equations. The pseudo-first-order equation, which is also known as the Lagergren model and the linear form of the equation, is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (6)$$

Where: q_t is the biosorption capacity at time t and k_1 is the first-order rate constant (min). The values of k_1 and q_e can be calculated from the slope and the intercept of plot between log (q_e-q_t) and t.

The pseudo-second-order, which is known as the Ho and McKey model and the linear form of the equation, is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

Where: k_2 is the second-order rate constant (g/mg/min). The values of q_e and k_2 can be calculated from the slope and intercept of plot between t/qt versus t.

The value of biosorption capacity $q_{e(cal)}$ determined using the first-order model was far lower than the experimental $q_{e(exp)}$ value. On the other hand, the value of biosorption capacity $q_{e(cal)}$ obtained from the second-order model was approximate to the experimental value more than the value of the first-order model. A comparison of the regression coefficient (R^2) between the first-order and second-order (Table 3) showed that biosorption process closely followed the pseudo-second-order (Fig. 6) better than the pseudo-first-order. Therefore, the rate-controlling step of the biosorption process may be due to the chemisorption involving valency forces through the sharing or exchange of electrons between the tapioca peel and Cd(II) ions (Ho, 2006).

Table 3 Kinetic parameters of pseudo-first-order and pseudo-second-order

Experiment	Pseudo-first-order			Pseudo-second-order		
$qe_{(exp)}$	$qe_{(cal)}$	k_1	R^2	$qe_{(cal)}$	k_2	R^2
4.32	1.49	0.058	0.9506	4.55	0.079	0.9998

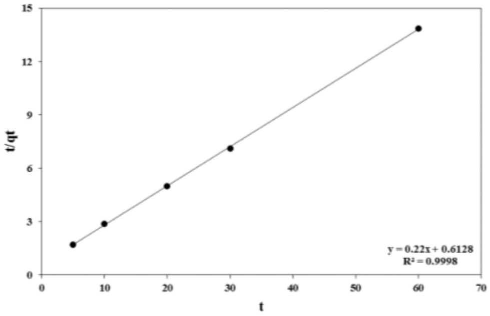

Figure 6 Pseudo-second order plots of Cd(II) onto tapioca peel

Biosorption thermodynamic

The effect of temperature is an important influencing factor in the biosorption process. The thermodynamic behaviour for biosorption of Cd(II) onto tapioca peel was mentioned at three different temperatures, viz., 15, 35, and 55 °C. The results showed that when the temperature increased from 15 to 55 °C, the biosorption capacity increased from 3.50 to 4.71 mg/g. The increases in capacity of Cd(II) with temperature may be due to the enlargement of pore size or the activation of some components available at the surface of tapioca peel that respond to Cd(II) biosorption (Ajmal et al., 2000). The thermodynamic distribution coefficient (KD) was expressed as in the following equation:

$$K_D = C_A/C_e \qquad (8)$$

Where: C_A is the equilibrium concentration on the surface of tapioca peel (mg/L).

The value of free energy change (ΔG°) was calculated from the following equation:

$$\Delta G° = -RT\ln K_D \qquad (9)$$

Where: R is the gas constant (8.314 J/mol/K) and T is the temperature (°K). The values of the entropy change (ΔS°) and enthalpy change (ΔH°) were obtained from the slope and intercept of the plot between ln K_D versus 1/T.

$$\ln \mathrm{K_D} = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{10}$$

The results showed that (Table 4) the value of ΔG° was calculated to be −1.99, −4.77, and −7.54 kJ/mol. The negative values of ΔG° confirm the spontaneous nature of Cd(II) biosorption. The values of ΔS° and ΔH° were found to be 138.9 J/mol and 38.03 kJ/mol. The positive value of ΔS° indicates that the freedom of Cd(II) ions is not too restricted in the tapioca peel. The positive value of ΔH° indicates that the biosorption of Cd(II) onto tapioca peel was the endothermic process.

Table 4 Thermodynamic parameters for the biosorption of Cd(II) onto tapioca peel

Temp (K)	ΔG°(kJ/mol)	ΔH°(kJ/mol)	ΔS°(kJ/mol K)	R^2
288.15	−2.98			
308.15	−5.02	26.41	0.102	0.9871
328.15	−7.06			

Organic functional groups analysis

The FTIR spectra of tapioca peel before and after the biosorption of Cd(II) were used to determine the frequency changes of the organic functional groups in the tapioca peel and the spectra wave number varying from 400 to 4000 cm^{-1}. The FTIR spectrum of native tapioca peel (Fig. 7A) showed the presence of several functional groups. The adsorption peak at 3431 cm^{-1} was attributed to the stretching vibration of the O–H bond due to alcohols, and the peak at 2929 cm^{-1} was likely due to the presence of C–H bonds in the carboxyl group. The peak observed at 1760 cm^{-1} was due to the stretching vibration of the C=O bond due to carboxylic acids (Feng et al., 2011). The peak at 1652 cm^{-1} might be attributed to the stretching of the C=C and C=O bonds, and the peak observed at 1031 cm^{-1} was attributed to the stretching of the C–O bond due to alcohols, carboxylic acids or esters. The FTIR spectrum of Cd-loaded tapioca peel (Fig. 7B), showed that the stretching vibration at 3431, 2929, 1760, 1652, and 1031 cm^{-1} were changed and shifted to 3421, 2925, 1745, 1631, and 1026 cm^{-1}, respectively. These shifts in the FTIR spectrum of tapioca peel after the biosorption of Cd(II) may be attributed to the chemical interactions, as the ion exchange between hydrogen atoms of hydroxyl and carboxyl groups of tapioca peel and Cd(II) ions were mainly involved in the biosorption of Cd(II) onto tapioca peel (Sari et al., 2008).

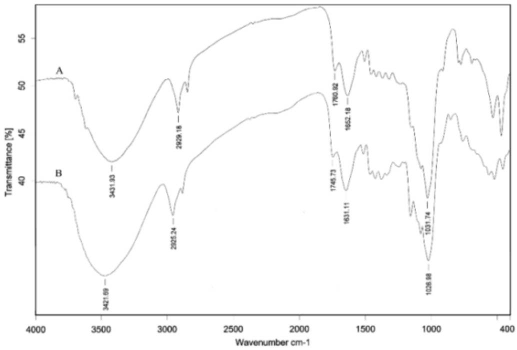

Figure 7 FTIR spectrum of tapioca peel (A) native tapioca peel
(B) Cd-loaded tapioca peel

Desorption and regeneration studies

The regeneration of biosorbent may be crucially important for keeping down the operating costs of heavy metal removal from wastewater. The results showed that the highest desorption efficiency of 86.73% was attained with 0.1 M HCl. Conversely, NaCl was less efficient than the other desorbing agents (Fig. 8). The inefficient desorption by NaCl was ascribed to the formation of alkaline metal complexes or metal precipitation at high pH (Saeed & Iqbal, 2003). The regeneration of tapioca peel was reused for up to six cycles using 0.1 M HCl as a desorbing agent (Fig. 9). In total, the biosorption capacity was slightly decreased by 6% after a sequence of six cycles. Meanwhile, the recovery of Cd(II) decreased from 88.74 to 70.91% in the sixth cycle. There is a reduction in both percentage biosorption and desorption. It may be concluded that HCl has the potential to desorbent the metal ions due to H^+ biosorption and pH shift, however, in turn, this also changes the functional chemistry of the surface leading to reduction in the capacity of the bio-adsorbent in next cycle (Gupta et al., 2022).

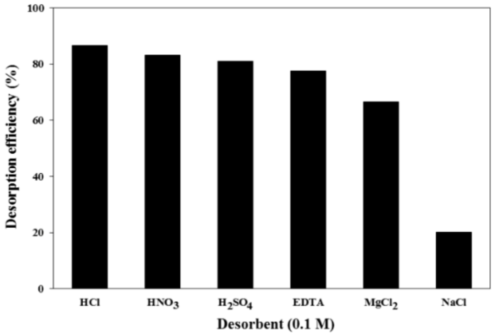

Figure 8 Effect of desorbent on the desorption of Cd(II) from tapioca peel

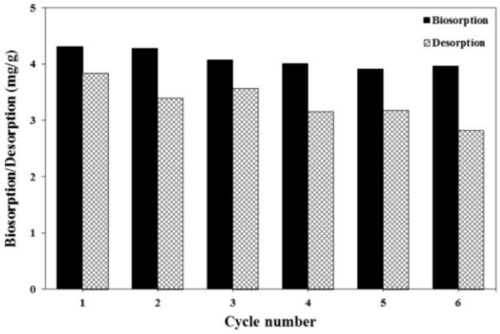

Figure 9 Six cycles of Cd(II) Biosorption-Desorption with 0.1 HCl

Conclusions

Cd(II) biosorption onto tapioca peel was found to be dependent on contact time, solution pH, initial concentration, and temperature. Langmuir isotherm described the biosorption of Cd(II) onto tapioca peel better than the Freundlich isotherm with a maximum biosorption capacity of 36.10 mg/g at an optimum pH of 5. The pseudo-second-order equation well-fitted the biosorption kinetics, and the thermodynamic behaviour indicated that the Cd(II) biosorption onto tapioca peel was an endothermic process. FTIR analysis revealed that carboxyl and hydroxyl groups were mainly responsible for the biosorption of Cd(II). Desorption studies showed that more than 86% desorption of Cd(II) was attained with 0.1 M HCl. Tapioca peel in this work has been shown to be greatly efficient and an alternative biosorbent for the biosorption and desorption of Cd(II) from aqueous solution because of its reasonable high biosorption capacity, and this waste is available in large quantities from tapioca starch industry in Thailand.

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