การดูดซับแคดเมียมจากสารละลายโดยเปลือกส้มโอ (*Citrus grandis*)

Adsorption of Cadmium from Aqueous Solutions by Pomelo Peel (*Citrus grandis*)

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บทคัดย่อ

งานวิจัยนี้ศึกษาการดูดซับแคดเมียมจากสารละลายโดยใช้เปลือกส้มโอ (PP) เป็นสารดูดซับ ซึ่งเป็นสารชีวมวลธรรมชาติที่มีอยู่ทั่วไปและมีราคาถูก คุณลักษณะเฉพาะของ PP ถูกวิเคราะห์ด้วยวิธี BET สเปกตร้าของ FT-IR และภาพถ่าย SEM ผลการวิเคราะห์แสดงให้เห็นว่า พื้นที่ผิวจำเพาะของ PP มีค่าเท่ากับ 0 m^2/g PP มีหมู่คาร์บอกซิลและหมู่ไฮดรอกซิลเป็นองค์ประกอบซึ่งทำหน้าที่ในการสร้างแรงยึดเหนี่ยวกับแคดเมียม และพื้นผิวของ PP มีรูพรุนขนาดกลางหรือขนาดใหญ่ จากนั้นทำการศึกษาปัจจัยที่มีผลต่อการดูดซับ ได้แก่ ค่าพีเอชเริ่มต้นของสารละลาย (pH_0) ความเข้มข้นเริ่มต้นของแคดเมียม เวลาสัมผัส และอุณหภูมิ พบว่า สภาวะที่เหมาะสมในการดูดซับได้แก่ pH_0 เท่ากับ 5.0 ความเข้มข้นเริ่มต้น 600 mg/L อุณหภูมิ 30 °C และเวลาในการดูดซับ 60 นาที โดยสามารถดูดซับได้ 263.60 mg/g ไอโซเทอมการดูดซับสอดคล้องกับสมการแลงเมียร์ และมีข้อมูลเชิงจลนพลศาสตร์สอดคล้องกับแบบจำลองจลนพลศาสตร์อันดับสองเทียม การเปลี่ยนแปลงพลังงานอิสระกิบส์และเอทาลปีมีค่าเป็นลบแสดงว่ากระบวนการดูดซับเกิดขึ้นได้เองและเป็นกระบวนการคายความร้อน การฟื้นฟูสภาพของ PP ที่ผ่านการดูดซับแคดเมียมแล้วสามารถทำได้โดยการชะด้วยน้ำกลั่นและสารละลายกรดไฮดรอคลอริก เข้มข้น 0.1 M จากผลการวิจัยข้างต้นชี้ให้เห็นว่า PP เป็นตัวดูดซับที่มีศักยภาพในการดูดซับแคดเมียมจากสารละลาย

คำสำคัญ : แคดเมียม เปลือกส้มโอ การดูดซับ การฟื้นฟูสภาพ

Abstract

This research studied the adsorption of cadmium from aqueous solutions by the use of pomelo peel (PP), a natural, locally available, and inexpensive biomass, as an adsorbent. The characteristics of PP were analyzed by the Brunauer-Emmett-Teller method, Fourier transform infrared spectroscopy, and scanning electron microscope (SEM) image. Results showed that the specific surface area of the PP was 0 m^2/g. The PP contained carboxylic and hydroxyl groups which were responsible for interaction with cadmium and the SEM image showed the external surfaces of PP were mesoporous or macroporous. The affecting factors, including initial solution pH (pH_0), initial cadmium concentration, contact time, and temperature, were investigated. It was found that the optimum condition was obtained under the condition: pH_0 of 5.0, 200 mg/L of initial concentration, 30°C, and 60 min with the adsorption capacity of 263.60 mg/g. The adsorption isotherm obeyed Langmuir equation. The kinetic data of the adsorption process conformed to the pseudo-second order kinetic model. The negative of standard Gibbs free energy change and enthalpy change revealed that the adsorption process was spontaneous and exothermic. The regeneration of cadmium-loaded PP can be done by leaching with distilled water and 0.1

M HCl. The results of this study indicated that the PP is an attractive candidate for the removal of cadmium from aqueous solutions.

Keywords: Cadmium; Pomelo peel; Adsorption; Regeneration

Introduction

Contamination of the environment by heavy metals occurs from many sources, including industrial, agricultural, and domestic. Cadmium is a heavy metal often detected in effluent from industries involved in mining, electro-plating, smelting, alloying, dyes, and batteries. The combination of cadmium and free radicals of hydroxyl, anion of superoxide, nitric oxide, and peroxide is carcinogen in humans' lungs, pancreas, prostate glands, and livers. Also, high amounts of cadmium accumulation in the kidneys causes serious damage to these organs and bones [1]. Thus there is a necessity to limit cadmium in wastewater.

Many wastewater treatments exist to remove cadmium from effluent, such as ion exchange, solvent extraction, chemical precipitation, membrane filtration, electrochemical methods, and adsorption [2, 3]. Although these methods are highly efficient, they have limitations, such as high chemical and energy consumption, high operating costs, and secondary pollutants [4, 5]. Therefore, environmental engineers and occupational health and safety staff investigated more efficient and less costly wastewater treatment methods. Biomaterials which can adsorb heavy metal ions are bacteria, fungi, algae, industrial waste, agricultural residues, and polysaccharides [6, 7]. Fruit peel is an abundant waste found in domestic situations and fruit juice industries. This material has a high amount of pectin which is composed of a functional carboxylic group.

Pomelo is a fruit which is widely grown and used in Thailand. Pomelo peel (PP) is composed of soluble and insoluble monomers and polymers [8]. The soluble parts are glucose, fructose, sucrose, and xylose, and the insoluble parts are pectin, cellulose, and hemicelluloses. These insoluble parts constitute between 50 and 70% of the whole material. These polymers have important functional groups such as carboxylic and hydroxyl groups which can interact with cations of heavy metals in aqueous solutions [9].

In this research, plentiful and cheap amounts of PP were used as a biosorbent to remove cadmium from aqueous solutions. The biosorbent was analyzed to determine the specific surface area, surface functional groups, and morphology. Factors such as the initial solution pH, initial cadmium concentration, contact time, and temperature were investigated. Equilibrium results were correlated with Langmuir and Freundlich equations. Kinetic data were fitted by pseudo-first and pseudo-second order kinetic models. Finally, reutilization of cadmium loaded on PP was studied by solvent elution such as distillated water and 0.1 M HCl.

Materials and Methods

1. Preparation of the biosorbent

The natural PP used in this work was obtained from a market in Warin Chamrap, Ubon Ratchathani Province, Thailand as solid waste. The yellow-green peel (flavedo) was removed from the PP with a knife. The residue of white spongy peel (albedo) was then washed with distilled water several times to remove all impurities. The washed material was cut into small pieces and naturally dried in the sun for 6 days. It was then ground into a powder by a blender and finally screened to obtain a particle size under 140 µm, and stored in a desiccator for further use. No other chemical or physical treatments were applied prior to the adsorption experiments.

2. Preparation of metal ion solutions

A stock solution of 1 g/L cadmium ions was prepared by dissolving an appropriate amount of $CdCl_2.5/2H_2O$ which has a molecular weight of 112.41 g/mol in distilled water. The concentrations used were obtained by dilution of the stock solution. The pH was adjusted to a given value by adding of HCl (1 M) and NaOH (1 M) and was measured using a Benchtop pH meter (700 EUTECH, Thermo Scientific). All chemicals used in the study were of analytical grade. Metal ion concentrations were determined using an Atomic Absorption Spectrophotometer (AA-650, Perkin Elmer). The calibration curve was constructed to convert the metal concentration and absorbance.

3. Biosorption experiments

All batch sorption studies were carried out by adding a fixed amount of sorbent (0.1g) into 250 mL Erlenmeyer flasks containing 100 mL of metal solutions. A series of adsorption experiments was performed in different operating conditions related to the initial solution pH, initial metal concentration, contact time, and temperature. The effect of the initial solution pH was carried out by varying the pH_0 of 50 mg/L cadmium solution from 2.0 to 6.0. Agitation was provided for 24 hr, sufficient to reach equilibrium with a constant agitation speed of 200 rpm and 30°C. The samples were measured and then filtered by micro-filter and then finally the metal concentrations in the filtrate were analyzed. The metal concentrations were measured at time t=0 and at equilibrium. The effects of initial metal concentrations were investigated in the same fashion as that in the first experiment, but the initial concentrations were varied in a range of 50 to 600 mg/L of metal solution (pH_0 = 5.0). The effects of contact time were investigated in the same manner as the first experiment but the pH_0 was fixed at 5.0. The samples were measured every 10 min during the first hour, then every 30 min during the second hour, and then finally every 1 hr until the final concentration reached a constant. Finally, the effects of temperature were investigated by varying the operating temperatures from 30 to 60°C with the initial metal concentration of 50 mg/L (pH_0 = 5.0).

4. Desorption experiments

The solution with initial cadmium concentration of 100 mg/L was adsorbed in the same manner as the effects of initial concentration experiment. A certain amount of cadmium-loaded PP was harvested from the suspension by filtrating with micro-filter and dried at 60°C until the weight was constant. The cadmium-loaded bisorbent was desorbed by adding a fixed amount of sorbent (0.1g) into 100 mL of distilled water or 0.1M HCl solution. The flasks were shaken at 200 rpm for 24 hr at 30°C. The samples were measured and then filtrated by micro-filter. The metal concentration in the filtrate was determined.

5. Characterization of biosorbent

The specific surface area was determined from N_2 adsorption-desorption isotherm at 77K by using an Automatic Surface Analyzer (ASI-C-8, Quantahrome Instrument). The specific total surface area was calculated using the Brunauer-Emmett-Teller (BET) equation. The surface functional groups of PP were detected by Fourier transform infrared spectroscope (FTIR-2000, Perkin-Elmer) to identify functional groups responsible for metal binding. The morphology of the PP was also analyzed by scanning electron microscope (SEM) image. The biosorbed quantity and the removed cadmium percentage (%Cd^{2+} Removal) were calculated using the following equations:

$$q_t = \frac{V(C_0 - C_t)}{m} \qquad (1)$$

$$\% \, Cd^{2+} Removal = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (2)$$

where q_t (mg/g) is the quantity of metal ions biosorbed per unit mass of biosorbent, C_0 (mg/L) is the initial metal ions concentration, C_t (mg/L) is the metal ions concentration after biosorption, m (g) is the mass of biosorbent, and V (L) is the volume of aqueous solution.

Results and Discussion

1. Characteristics of biosorbent

N_2 adsorption-desorption isotherm at 77K is depicted in Fig. 1. The isotherm was in accordance with type III isotherm of the International Union of Pure and Applied Chemistry (IUPAC) describing adsorption of nonporous or macroporous adsorbent with weak adsorbate-adsorbent interactions which may provide multilayer adsorption [10]. The specific surface area of PP adsorbent obtained by multipoint BET analysis was approximately 0 m^2/g. Furthermore, the external surface area and micro pro surface area were also 0 m^2/g. According to IUPAC, pores are classified as micropores (less than 2 nm diameter), mesopores (2-50 nm diameter), and macropores (more than 50 nm diameter). The average pore diameter determined by Barrett-Joyner-Halenda (BJH) method was found to be 3.96 nm, indicating that mesopores are the main part of the adsorbent.

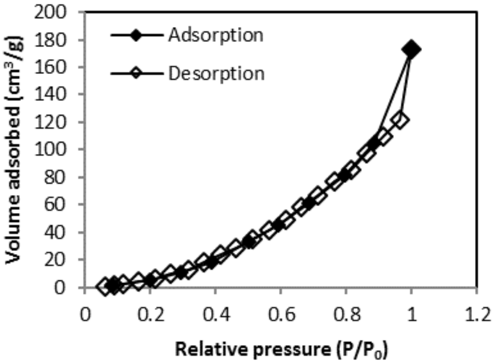


Fig. 1 N_2 Adsorption and desorption isotherm of PP at 77 K

The chemical structure of the biosorbent is of vital importance in understanding the adsorption process. The FT-IR technique is an important tool to identify the characteristic functional groups which are instrumental in adsorption of metal ions. The FT-IR spectrum of the PP adsorbent is shown in Fig. 2. From this spectrum, it was observed that the PP contained a large number of functional groups which constituted this biosorbent material. In PP, absorption peaks around 3,500-3,300 cm^{-1}, the O-H stretching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds such as alcohol and phenols, and carboxylic acids, as in pectin, cellulose, and lignin, thus showing the presence of free hydroxyl groups on the adsorbent surface [11]. The peaks at 2,919 cm^{-1} were attributed to the symmetric and asymmetric C-H stretching vibration of aliphatic acids. The peak at 1,737 cm^{-1} was due to the stretching vibration of bond due to non-ionic carboxyl groups (-COOH, -COOCH$_3$), and may be assigned to carboxylic acids or their esters [12]. The peaks around 1,616 and 1,418 cm^{-1} were due to asymmetric and symmetric stretching vibrations of CO in ionic carboxylic groups (-COO$^-$) respectively [13]. Aliphatic acid group vibration at 1,261 cm^{-1} may be attributed to deformation vibration of C=O and stretching formation of –OH of carboxylic acids, and phenols. The strong band at 1,068 cm^{-1} can be allocated to the C-O of alcohols and carboxylic acids [14]. The peaks found between 1,130-1,000 cm^{-1} were due to the vibration of C-O-C, C-O-P, and O-H of polysaccharides [15]. The IR-spectra result showed that carboxylic and hydroxyl groups were responsible for the binding of cadmium.

The SEM analysis of PP revealed important information about the surface morphology. As seen in Fig. 3, the biosorbent has some cavities in its structure capable of up-taking metal ions. According to the results interpreted from N$_2$ adsorption–desorption isotherm, the complex and porous surface texture was expected due to the existence of mesopores and macropores on the PP surface.

2. Effects of initial solution pH

pH plays an important role in the bio-sorption process of the metal ions which affects the solubility of the metal ions, concentration of counter ions on the functional groups of the adsorbent, and the degree of ionization of the adsorbate during the reaction. These have been studied by many researchers [16-18]. Biosorption was low at strong acidic medium and percent Cd^{2+} removal of PP increased with an increase in the initial solution pH, until a certain value was reached. As shown in Fig. 4, the minimum percent removal was at pH 2.0 (0.72%), increased up to 4.0 (42.83%), and remained nearly.

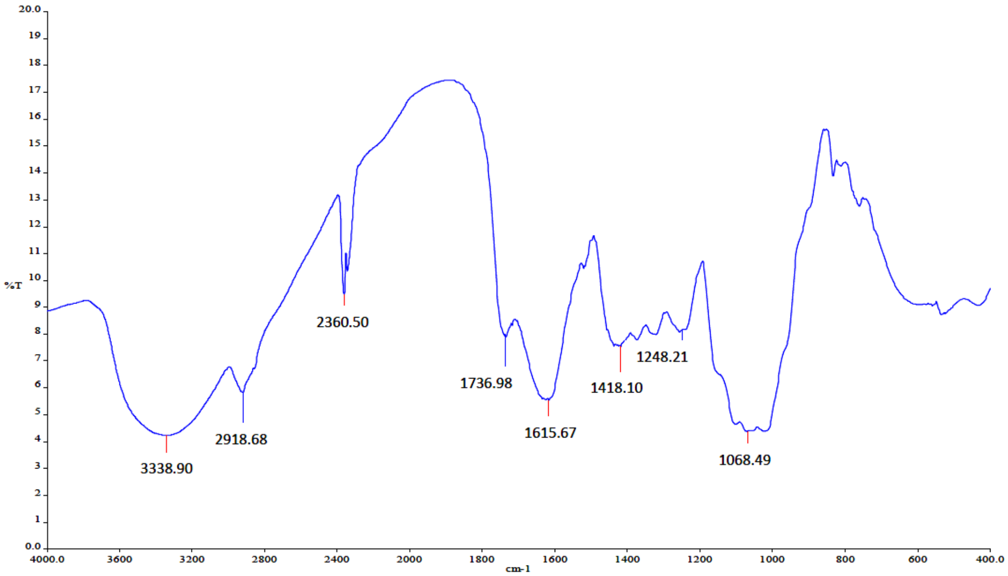


Fig.2 FT-IR spectroscopy of PP

[19].

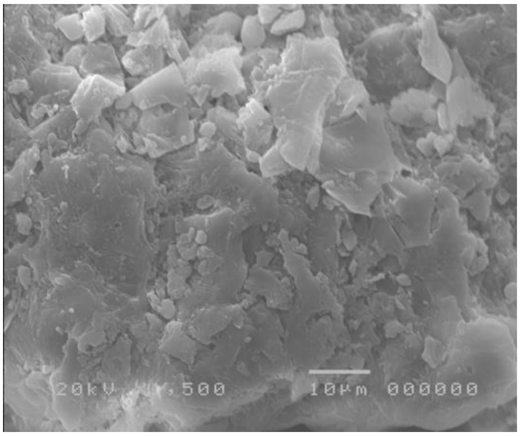


Fig. 3 SEM micrographs for PP

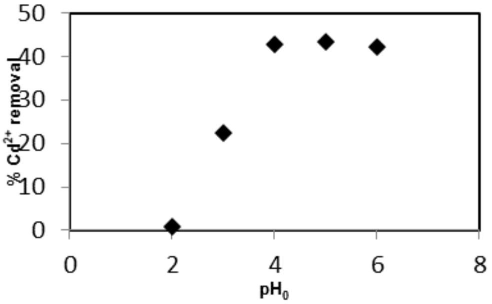
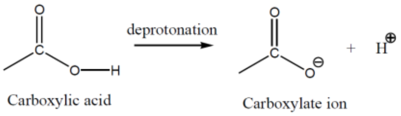


Fig.4 Effects of initial solution pH on the percent cadmium removal of PP (C_0 = 50 mg/L, temperature 30°C, stirring rate 200 rpm for 24 hr and m = 0.1 g)

constant over the initial pH range of 5.0 to 6.0. A pH value of 5.0 was chosen as being the optimum for further experiments to avoid the precipitation of $Cd(OH)^{2+}$ as Cd^{2+} precipitates above pH 6.0 in the form of $Cd(OH)_2$ and biosorption cannot take place [18]. The carboxylic group is active binding sites which cause the interaction with cadmium. The carboxylic groups present in the adsorbent have the pKa values from 3.0 to 5.0. Therefore, at higher pH, deprotonation occurs as shown in equation (3) [19].



(3)

Carboxylate ions released and resulted in more interaction between the negatively-charged carboxylate anions and positively-charged cadmium species [20]. Preliminary FT-IR indicated inter- and intra-molecular hydrogen bonding of alcohols, carboxylic acids, and phenols showing the presence of “free” hydroxyl groups on the adsorbent surface [21]. Hydrogen bonding for the adsorption process was due to the –COOH groups and –OH groups as shown in equations

(4) and (5) [19, 20]. R is the matrix of the biosorbent.

$$2(ROH) + Cd(OH)_2 \longrightarrow (\text{-}ROH)_2\_Cd(OH)_2 \qquad (4)$$

$$(RCOOH) + Cd(OH)_2 \longrightarrow (\text{-}RCOOH)_2\_Cd(OH)_2^- \qquad (5)$$

At pH 2.0, a very low percent metal removal was observed because functional groups such as free carboxylic and hydroxyl groups were not dissociated. Lower adsorption of cadmium at acidic pH was probably due to the competition between H^+ and metal cations of cadmium for the exchangeable sites on the biosorbent, thereby partially releasing the cations which resulted in very low cadmium uptake. As surface charge density decreased with an increase in the solution pH, the electrostatic repulsion between the positively-charged metal (cadmium) and the surface of the PP was lowered, which may result in an increase in the rate of adsorption. A similar result was reported for the adsorption of cadmium as those in the literature [21, 22]. At a higher solution pH, the PP may become negatively-charged, which enhanced the positively-charged metal cations through electrostatic forces of attraction.

3. Effects of initial metal concentration and contact time

The metal uptake increased with increases in the cadmium initial concentration in solution to the highest adsorption capacity of 263.60 mg/g at the initial concentration of 600 mg/L as shown in Fig. 5. This can be attributed to the plentiful binding sites on the adsorbents. The further increase of higher adsorption capacity (C_0>600 mg/L) was expected if higher initial cadmium concentrations were assigned.

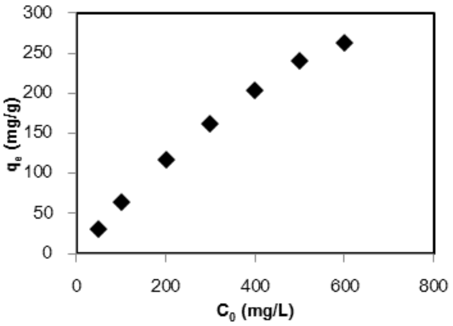


Fig. 5 Effects of initial concentration on the adsorption of cadmium onto PP (C_0 = 50-600 mg/L, pH_0 = 5.0, temperature 30°C, stirring rate 200 rpm for 24 hr and m = 0.1g)

Contact time is a fundamental parameter in all transfer phenomena of biosorption. To establish the equilibrium time for maximum uptake of cadmium, the biosorption of cadmium on the biosorbent was studied as a function of contact time. The adsorption capacity of cadmium onto PP increased with increases in contact time as depicted in Fig. 6. It was observed that the sorption rate was rapid during the first 5 min, and then the rate was slower during the 5 to 60 min range, and a plateau was reached after 60 min. It can be stated that the rapid rate in the initial stage was due to more available active sites on the outer and inner surfaces of the adsorbent, and the slower rate in the later stage was due to less availability on the outer surfaces and slower diffusion of metal ions into the interior of the adsorbent. The plateau adsorption capacity at the final stage indicated that the adsorbent reached saturation with the metal ions at 60 min which was the sorption equilibrium time. The rapid kinetics has significant practical importance, as it facilitates smaller reactor volumes, ensuring high efficiency and economy [23]. The experiments were performed in a high agitation speed system in which all the binding sites were readily available for metal sorption, and hence the effect of external diffusion cannot be considered as a limiting step. Equilibrium attained in a relatively short contact time indicated that the adsorption of cadmium was a controlled chemical reaction rather than a diffusion-controlled process. There was no significant change in the uptake of cadmium by the biosorbents after about 60 min. This was due to saturation of the adsorbent by the cadmium [24].

Although the equilibrium stage was achieved within 60 min, the stirring time for equilibrium experiments was assigned as 24 hr to ensure complete metal adsorption which was well documented [2, 6, 8 and 12].

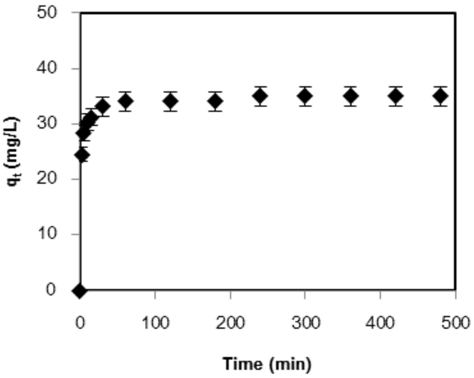


Fig. 6 Effects of contact time on the adsorption of cadmium onto PP (C_0 = 50 mg/L, pH_0 = 5.0, temperature 30°C, stirring rate 200 rpm and m = 0.1g)

4. Effects of temperature

The increase of temperature in the system caused a decrease of the adsorption capacity as shown in Fig. 7. This indicated that the reaction was an exothermic process. This result was in accordance the literature [25, 26]. Thermodynamic parameters can be determined from the variation of the thermodynamic equilibrium constant K_0 with temperature.

For adsorption reactions, K_0 is defined as follows:

$$K_0 = \frac{\gamma_S C_S}{\gamma_e C_e} \tag{6}$$

where C_s is the surface concentration of cadmium (mmol/g), C_e is the cadmium concentration in solution at equilibrium (mmol/ml), and γ_s and γ_e are activity coefficients of the adsorbed cadmium and cadmium in solution respectively. The expression of K_0 can be simplified by assuming that the concentration in the solution approaches zero resulting in $C_s \longrightarrow 0$ and $C_e \longrightarrow 0$ and the activity coefficients approach unity at these very low concentrations [27]. Eq.6 can be written as:

$$\lim_{C_S \to 0} \frac{C_S}{C_e} = \frac{C_S}{C_e} = K_0 \tag{7}$$

The adsorption standard free energy change (ΔG^0) can be calculated from:

$$\Delta G^0 = -RT \ln K_0 \tag{8}$$

where R is the universal gas constant (8.314 J/mol.K) and T is temperature in Kelvin. The average standard enthalpy change (ΔH^0) and the standard entropy change (S) are determined from the Van't Hoff equation [27].

$$\ln K_0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{9}$$

The values K_0 of cadmium adsorption on PP evaluated were 826.82, 770.12, 658.19 and 492.24 for 30, 40, 50, and 60°C respectively. All thermodynamic parameters of cadmium adsorption on PP and enthalpy change of -14.24

kJ/mol of PP obtained in this study indicated that the adsorption system was exothermic. The negative value of ΔG^0 confirmed the feasibility of the spontaneous nature of adsorption. This also confirmed the possibility of physical adsorption. The positive value of entropy change (ΔS^0) corresponded to an increase in the degree of freedom of the adsorbed species. A small change in the entropy showed that the PP did not significantly change.

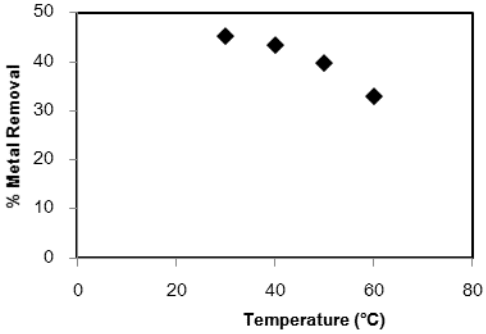


Fig. 7 Effects of temperature on the adsorption of cadmium onto PP (C_0 = 50 mg/L, pH_0 = 5.0, temperature 30-60°C, stirring rate 200 rpm for 24 hr and m = 0.1g)

5. Adsorption isotherms

The study of adsorption isotherms is fundamental, and plays an important role in the determination of the maximal capacity of adsorbent. The equilibrium data usually were correlated by well-established isotherm models such as Langmuir and Freudlich isotherms. For the adsorption on a totally homogeneous surface, generally the Langmuir equation applies because here interactions between adsorbed molecules are negligible. The Langmuir equation is most often used to describe equilibrium sorption isotherm [27] which is valid for monolayer sorption with a finite number of identical sites. The linear form of Langmuir isotherm is given below:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad (10)$$

where q_m (mg/g) is the maximum sorption of monolayer, C_e (mg/L) is a final equilibrium concentration of cadmium, q_e (mg/g) is the cadmium adsorbed per unit weight of the PP at final equilibrium concentration, and K_L (ml/g) is the Langmuir constant related to the affinity of binding sites.

The essential characteristics of the Langmuir isotherm can be expressed by means of "R_L" which is a dimensionless constant referred to as a separation factor of equilibrium parameter. The R_L is defined by:

$$R_L = \frac{1}{1 + K_L . C_0} \qquad (11)$$

This parameter suggests the type of isotherm is irreversible ($R_L=0$), favorable ($0<R_L<1$), linear ($R_L=1$), or unfavorable ($R_L>1$). As can be seen from Table 1, the R_L values are between 0 and 1.0, indicating that the adsorption of cadmium onto PP is favorable.

The widely used empirical Freundlich equation based on sorption on a heterogeneous surface is given by:

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e) \qquad (12)$$

where K_F ($mg^{1-1/n}.L^{1/n}.g^{-1}$) and n are the physical constants of the Freundlich isotherm. The K_F and n are the indicators of adsorption capacity and adsorption intensity respectively [28].

The results showed the Langmuir isotherm was best fitted to the experimental data for cadmium indicating that the monolayer of cadmium molecules covered along the PP surface. Table 1 shows that the monolayer capacity of absorbed cadmium onto PP was 434.78 mg/g.

Table 1 Isotherm constants and correlation coefficients for the adsorption of cadmium on PP

Isotherm model	Parameters	Value
Langmuir	q_m (mg/g)	434.78
	K_L (l/mg)	4.57×10^{-3}
	R^2	0.9945
	R_L	0.27
Freundlich	K_F (l/g)	3.87
	n	1.34
	R^2	0.9796

6. Adsorption kinetics

To find the mechanism controlling the adsorption process, pseudo-first-order, pseudo-second order, and intraparticle diffusion models were used to check the experimental data. The q_t (mg/g) is the amount of cadmium adsorbed at time t.

The pseudo-first order kinetic model is normally applicable for only the initial 30 min of adsorption process. If the diffusion rate of adsorbate across the boundary layer is at a rate of limiting step, the kinetic data are well fitted to the pseudo-first order model [29]. It is generally expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (13)$$

where k_1 (min^{-1}) is the rate constant of first-order adsorption.

The pseudo-second order kinetic model was proposed by Ho in 1995 [30]. If the chemical sorption is the rate of limiting step, the experimental data follow the pseudo-second order expression according to Eq. (14). It is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (14)$$

where k_2 (min^{-1}) is the rate constant of second-order adsorption.

If the diffusion of cadmium ions into the pores and capillaries of the adsorbent is the rate of limiting step, the adsorption data can be presented by the following Eq. (15):

$$q_t = k_p . t^{1/2} + C \qquad (15)$$

where k_p represents intraparticle diffusion rate constant (mg/(g.min$^{1/2}$)) and C is a constant (mg/g) which gives information on the thickness of the boundary layer.

The calculated values of $q_{e,cal}$ (Table 2) from the pseudo-first-order kinetics model and intraparticle diffusion model were dramatically lower than the experimental value (q_{exp}). The linear plot of t/q_t against t according to Eq. (14) was observed. The constant k_2 and the corresponding linear regression correlation coefficient values, R^2, are given in Table 2. As the values of R^2 were limited to unity (0.9986), the adsorption data conform to the pseudo-second order model. This indicated that the rate of limiting step was the formation of chemical bonding between the cadmium ions and the dissociated functional groups on the surface of the PP.

Table 2 Pseudo-first order, pseudo-second, and intra-particle diffusion kinetic parameters for cadmium adsorption on PP

Kinetic model	Parameters	Value
	$q_{e,exp}$(mg/g)	35.02
Pseudo-first order	k_1 (min^{-1})	2.67 x10^{-2}
	$q_{e,cal}$ (mg/g)	9.12
	R^2	0.8687
Pseudo-second order	k_2 (g/(mg*min))	1.62 x10^{-2}
	$q_{e,cal}$ (mg/g)	35.09
	R^2	0.9999
Intraparticle diffusion	k_p (mg/(g.$min^{1/2}$))	0.74
	C (mg/g)	22.85
	R^2	0.3729

7. Desorption study

After desorption, the desorption efficiencies were 44.18% and 68.06% by using distilled water and 0.1 M H_2SO_4 as leashing solvent respectively. A complete desorption of cadmium ions could not be obtained, which may be due to cadmium ions becoming trapped in the intrapores and, therefore, difficult to release [31]. An interaction between cadmium and PP surface is weak as a physisorbed molecule usually can be easily desorbed. As the distilled water and acid solution can desorb the cadmium, it could be said that the attachment of the cadmium onto the adsorbent involved both physical and chemical processes.

Conclusion

PP can be used as a biosorbent for the adsorption of cadmium from aqueous solutions since the cell wall of PP is composed of pectin which contains free carboxylate and hydroxyl functional groups. These functional groups could be active sites for binding with cadmium by means of covalent bonding and/or electrostatic interaction. The results showed that the highest adsorption capacity of 263.60 mg/g was observed at pH of 5.0 and 60 min. Equilibrium data follow the equation of Langmuir and the kinetic data conform to pseudo-second order kinetic models. The cadmium uptake decreased with increases in solution temperature indicating an exothermic reaction. The regeneration of cadmium loaded PP can be done by using distilled water and 0.1 M H_2SO_4. Results of this study suggested that the PP is a reliable and dependable adsorbent with a promising potential for the removal of cadmium normally found in industrial effluents.

Acknowledgements

This study was financially supported by the Environmental Engineering Program in the Department of Chemical Engineering, Faculty of Engineering, Ubon Ratchathani University (UBU). The authors express their gratitude to the staff of the Office of International Relations at UBU for assistance with English.

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