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DURIAN PEEL AS BIOSORBENT FOR REMOVAL OF CADMIUM IONS FROM AQUEOUS SOLUTION

เปลือกทุเรียน-ตัวดูดซับทางชีวภาพเพื่อกำจัดแคดเมียมไอออนจากสารละลายเจือจาง

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Abstract

The ability of durian peel to remove Cd(II) ions from aqueous solution by biosorption was investigated. The sorption capacities at different solution pH, agitation speed, temperatures, initial cadmium ions concentrations and contact time were evaluated on a batch scale basis. At pH 5 and agitation speed 150 rpm, the cadmium ions removal reached at a maximum value. Increases in cadmium capacity with increasing temperature indicated endothermic nature of the biosorption process. The equilibrium was better described by the Langmuir isotherm model, with a maximum biosorption capacity of 18.55 mg/g. The biosorption was relatively quick about 15 min to reach the equilibrium. Biosorption kinetics followed a pseudo-second-order model. Desorption experiments indicate that the desorption efficiency using 0.1 N HCl, HNO_3 and H_2SO_4 aqueous solution were 96.58, 89.90 and 85.92%, respectively. Fourier Transform Infrared Spectroscopy revealed that carboxyl, hydroxyl, and amide groups on the durian peels' surface involved in the adsorption of the cadmium ions as well as morphological aspects. Biosorption by durian peel has potential to serve as a remover of Cd (II) from wastewater.

Keywords: Durian peel, Biosorption, Cadmium ions, Agricultural waste

บทคัดย่อ

ศึกษาความสามารถของเปลือกทุเรียนในการกำจัดแคดเมียมไอออนจากสารละลายเจือจาง โดยประเมินจากประสิทธิภาพดูดซับ ณ พีเอช ความเร็วรอบการเขย่า อุณหภูมิ ความเข้มข้นแคดเมียมไอออนเริ่มต้น และระยะเวลาในการดูดซับต่างๆ ในระดับแบช ที่พีเอช 5 และค่าความเร็วรอบการเขย่าที่ 150 รอบ/นท. แคดเมียมไอออนถูกกำจัดมากที่สุด ประสิทธิภาพดูดซับเพิ่มขึ้นเมื่ออุณหภูมิเพิ่มขึ้น แสดงให้เห็นว่ากระบวนการดูดซับทางชีวภาพที่เกิดเป็นการดูดซับความร้อนตามธรรมชาติ

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สมดุลอธิบายได้ดีด้วยโมเดลแลงเมียร์ไอโซเทอม ซึ่งให้ค่าการดูดซับสูงสุดที่ 18.55 มก./ก. การดูดซับทางชีวภาพเกิดขึ้นค่อนข้างเร็ว ประมาณ 15 นท. จึงถึงจุดสมดุล การทดลองการคายออกชี้ว่ามีประสิทธิภาพเท่ากับ 96.58, 89.90 และ 85.92% เมื่อใช้กรดไฮโดรคลอริก กรดไนตริก และกรดซัลฟุริก เข้มข้น 1 N ตามลำดับ ผลจากเครื่องเอฟทีไออาร์เปิดเผยว่า ไฮดรอกซิล คาร์บอกซิล และเอไมด์ ในผิวเปลือกทุเรียนมีส่วนเกี่ยวข้องกับการดูดซับแคดเมียมเช่นเดียวกับลักษณะทางสัณฐานวิทยา การดูดซับทางชีวภาพของเปลือกทุเรียนมีศักยภาพในการเป็นตัวกำจัดแคดเมียม (II) จากน้ำเสีย

คำสำคัญ: เปลือกทุเรียน, การดูดซับทางชีวภาพ, แคดเมียมไอออน, ของเสียทางการเกษตร

Introduction

Cadmium, a non-essential and non-beneficial element to plants and animals, is non-biodegradable and transferable through the food chain. Waste streams from electroplating, smelting, alloy manufacturing, pigments, plastic, batteries, mining and refining processes are major sources of cadmium release into the environment(1). Cadmium is a highly toxic environmental contaminant as well as its slow degradation presents a serious environmental problem. Therefore, it is necessary to alleviate cadmium ion from those industrial effluents. Many existing methods for treatment include chemical and surface chemistry processes such as precipitation, adsorption, membrane processes, ionic exchange, floatation, and others(2, 3). However, those techniques have their own inherent limitation such as less efficiency, sensitive operating conditions, and production of secondary sludge which further disposal is a costly affair(4). One such alternative is biosorption(5), where certain types of biomass are able to bind and concentrate metals from even very dilute aqueous solution. Biosorbents could be alternatives of the conventional sorbents(6). Several investigations have been carried out to identify suitable and relatively low-cost biosorbents that are capable of removing significant quantities of ions.

Several potent cadmium ions biosorbents under the class of agricultural wastes including orange wastes(7), olive stones(8), papaya wood(9), grape stalk waste, peas, broad bean, and medlar peels(10), lemon peels, orange peels, grapefruit peels, apple peels, apple kernel, apple core, and grape skins(11), coconut shell powder(12), coconut copra meal(13) were used and investigated. The emerging process of 'biosorption' uses nonviable or viable biological materials to bind contaminants via physico-chemical mechanisms, whereby factors like pH, size of biosorbent, ionic strength and temperature could affect metal biosorption. Most of the studies showed that these agricultural wastes are highly efficient for the removal of cadmium ions. Agricultural by-products usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups. These groups have ability to some extent to bind heavy metal ions by donation of an electron pair from these groups to form complexes with the metal ions in solution[14].

Durian peel was selected because of its abundance as an agricultural by product which rarely found any use. The purpose of this study was to explore the feasibility of using durian peel for cadmium ion removal from aqueous solutions by conducting batch experiments at variation of solution pH, agitation speed, temperature, initial cadmium ions concentration and contact time.

Materials and Methods

Biosorbent preparation

Durian peel was collected as solid waste then treated by washing with deionized water. The washed material was cut into small pieces (1-2 cm) then dried in a hot air oven (Memmert Model 600) at 60°C until they reached a constant weight, which was accomplished after 48 h In the final stage, it was dried, ground and sieved at the size of 150-212 μm.

In order to identify the active sites of cadmium binding, durian peel material before and after sorption experiment was analyzed with a FT-IR (Perkin Elmer System 2000) spectrometer under ambient conditions. To confirm surface condition of the biomass, scanning electron microscopy (SEM) photographs were taken on a JEOL JSM-5410 LV model.

Batch Biosorption Experiments

1) The effect of solution pH

The effect of initial solution pH was determined using solution pH ranging 1 to 6 and agitating 0.1 g durian peel and 100 ml $Cd(NO_3)_2.4H_2O$ solution at the concentration of 50 mg/l using a shaker. Agitation contact time was kept for 24 h, which is sufficient to reach equilibrium with a constant agitation speed of 150 rpm at 25°C. The pH was adjusted by adding 0.1 N NaOH or 0.1 N HNO_3 before and during each experiment.

2) The effect of agitation speed

The effect of agitation speed was determined by the agitation of 0.1 g durian peel and 100 ml $Cd(NO_3)_2.4H_2O$ solution at the concentration 50 mg/l using a shaker at solution pH 5. Agitation contact time was kept for 24 h, which is sufficient to reach equilibrium with a different agitation speed ranging from 0-300 rpm at 25°C.

3) The effect of temperature

The effect of temperature was determined by the agitation of 0.1 g durian peel and 100 ml $Cd(NO_3)_2.4H_2O$ solution at the concentration of 50 mg/l using a shaker at solution pH 5. Agitation contact time was kept for 24 h, which is sufficient to reach equilibrium with a constant agitation speed at 150 rpm at different temperature ranging from 25 to 55°C.

4) Isotherm experiments

The equilibrium isotherms were determined by the agitation of 0.1 g durian peel with a range of different concentration of $Cd(NO_3)_2.4H_2O$ solution 25 to 50 mg/l using a shaker at solution pH 5. Agitation contact time was kept for 24 h, which is sufficient to reach equilibrium with a constant agitation speed at 150 rpm at 25°C.

5) Kinetic experiments

The kinetic isotherms were determined by the agitation of 0.1 g durian peel with 100 ml $Cd(NO_3)_2.4H_2O$ solution at the concentration 50 mg/l using a shaker for difference contact times ranging from 2 to 240 min with a constant agitation speed, 150 rpm at 25°C.

6) Desorption experiments

In the batch desorption experiments were conducted using 250 ml erlenmeyer flasks containing 100 ml 0.1 N of HCl, HNO_3 and H_2SO_4 aqueous solution, and were contacted with cadmium ion-loaded biosorbents (0.1 g) at 25°C. These erlenmeyer flasks were placed in an incubator shaker operated 150 rpm for 24 h. After that, biosorbents were separated from the solution and the filtrate was subjected to residual metals concentration determination.

7) Cadmium analysis

After the biosorption experiment, the biosorbent was separated from the solution by filtering through a Whatman (0.45 μm GF/C) filter paper and the filtrate was analyzed for the cadmium ions concentration. The cadmium ions concentrations before and after the biosorption were determined by using Flame Atomic Absorption Spectrophotometer (Perkin Elmer Analyst 200). The pH values were adjusted by using 0.1 N NaOH or 0.1 N HNO_3 solutions. The pH was measured by using a pH meter (WTW. inoLab pH level 1).

The cadmium ions sorption capacity of durian peel was determined by employing the mass balance. The equilibrium cadmium ions sorption capacity could be calculated as

$$q_e = V(C_i - C_e)/m \quad (1)$$

Where qe is the equilibrium cadmium ions sorption capacity (mg/g), V is the suspension volume (l), m is the mass of durian material (g), C_i is the initial cadmium ions concentration (mg/l) and C_e is the cadmium ions concentration at the equilibrium (mg/l).

Result and Discussion

Effect of operating variables

The pH of the aqueous solution is an important parameter in the biosorption process(15). Effect of pH solution on the biosorption of cadmium ions to the durian peel was studied and results are shown in Figure 1. According to several authors(16, 17) the biosorption below pH 2 was slightly due to the competition of hydrogen ions for the active sites. It is clear that cadmium ions were effectively adsorbed in the pH 4-6 and the maximum biosorption of cadmium ions on durian peel materials occurred at pH 5. In contrast, researchers described that increasing of pH causes the formation of anionic hydroxide complexes, thus decreases the concentration of free cadmium ions, therefore, the biosorption capacity of cadmium ions was decreased[18]. The maximum biosorption of cadmium ions on durian peel material occurred at pH 5. The dependence of cadmium capacity on pH was similar to those sorption with the cadmium ion sorption on *Hydrilla verticillata* and Cystine-modified biomass[19, 20]. Therefore, all the subsequent experiments were performed with this optimum solution pH.

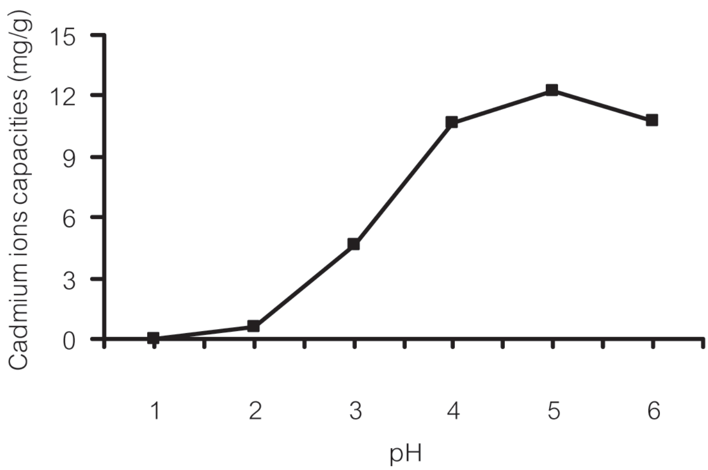

Figure 1 Effect of pH on the biosorption of cadmium ions onto durian peel

The effect of agitation speed on the biosorption is present in Figure 2. This effect may be attributed to the decrease in boundary layer thickness around the adsorbent particles that results from increasing the degree of mixing. However, when the shaking speed increased above 150 rpm, the diffusion speeds decreased. This may occur because the high shaking speed provided the sufficient additional energy to break newly formed bonds between the metal ions and the adsorbent surface[4]. Similar behavior has been reported by other researchers[21].

The effect of temperature on the biosorption is present in Figure 3. The increase of biouptake with increasing temperature had confirmed the endothermic nature of the biosorption process, which the desolvaton of the sorbing species and the change of the pore size.[22]

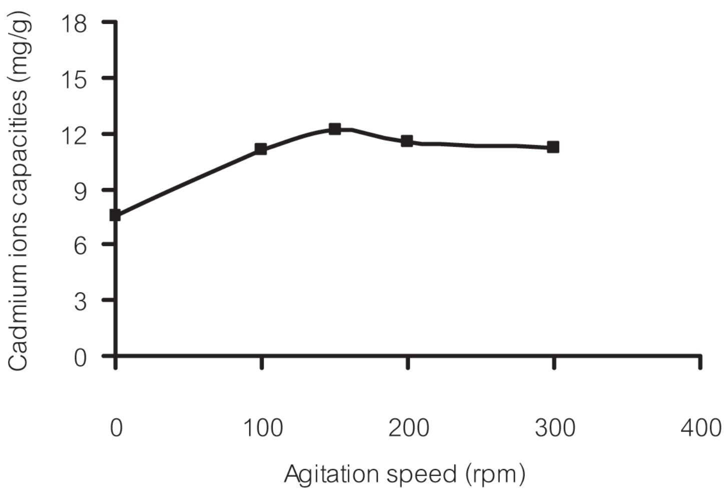

Figure 2 Effect of agitation speed on the biosorption of cadmium ions onto durian peel

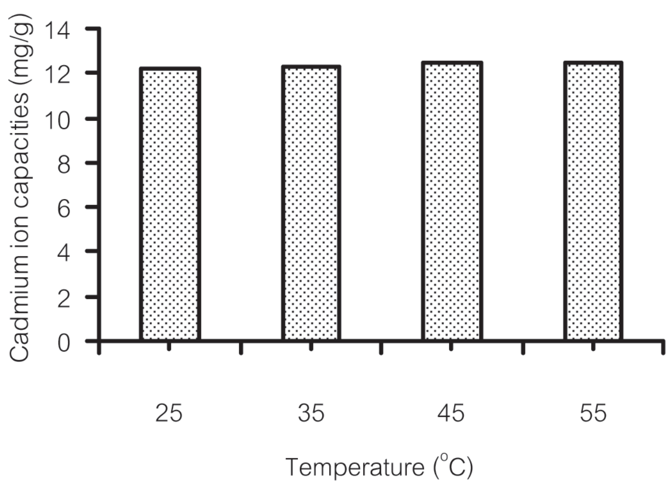

Figure 3 Effect of temperature on the biosorption of cadmium ions onto durian peel

Biosorption isotherms

Biosorption isotherms can be generated based on numerous theoretical models where Langmuir and Freundlich models are commonly used to fit experiment[23, 24]. Langmuir isotherm is presented by the following equation:

$$q_e = (q_{max} b C_e)/(1+bC_e) \quad (2)$$

And the Freundlich isotherm has the form

$$q_e = K_F C_e^{1/n} \quad (3)$$

Where q_e and q_{max} are the equilibrium and maximum sorption capacities (mg/g biosorbent), C_e is the equilibrium concentration (mg/l solution), b is the equilibrium constant, K_F and n are Freudlich constants characteristic of the system.

The linearization of Langmuir and Freudlich isotherms for the biosorbent experiments are presented in Figures 4 and 5 respectively. The models parameters are tabulated in Table 1. The experimental data could fit the Langmuir isotherm better than the Freudlich isotherm. This result indicates that the sorption of cadmium ions occurs on a homogenous surface by monolayer sorption without any interaction between adsorbed ions. In addition, the comparison of the maximum biosorption capacities for cadmium ions obtained the maximum biosorption capacity for cadmium ion is obtained in this study using different low-cost biosorbents reported in the literature. The results shows that the biosorption capacity of cadmium ion by the durian peel is greater than those found by using other biosorbents as listed in Table 2.

Table 1 Langmuir and Freundlich isotherm constants for cadmium ions biosorption onto durian peel

Langmuir model			Freundlich model		
b (l/g)	q_{max} (mg/g)	R^2	k_f (mg/l)	n	R^2
0.26	18.55	0.99	7.11	4.28	0.81

Table 2 Biosorption capacities for cadmium ions using different biosorbents

Biosorbent	Biosorption Capacity (mg/g)	Reference
Durian peel	18.55	This study
Papaya wood	17.22	(9)
Cystine-modified	11.63	(25)
H. verticillata	15.00	(19)

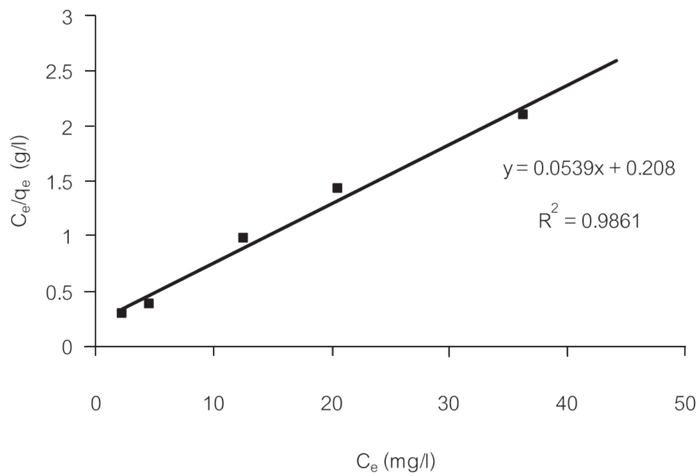

Figure 4 Linearization of Langmuir model for durian peel

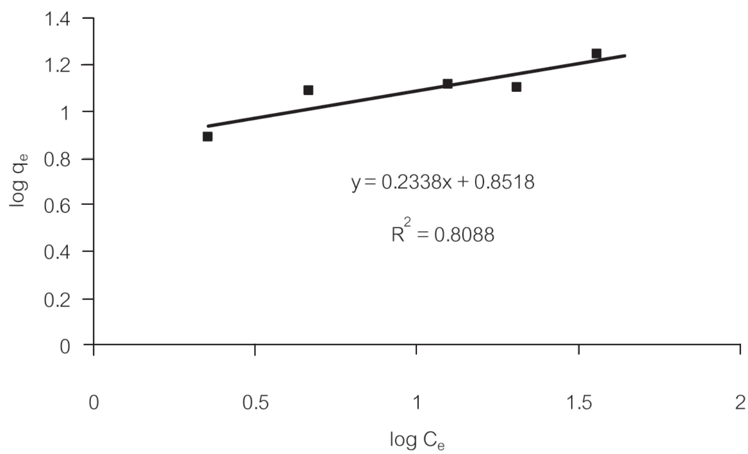

Figure 5 Linearization of Freundlich for durian peel

Biosorption kinetics

Various models have been used to analyze the kinetics of the sorption process. The pseudo-first-order rate equation of the Lagergren is one of the most widely used for the biosorption of solutes from a liquid solution[16, 26] and is represented as

$$\ln (1-q_t/q_e)= -k_1 t \quad (4)$$

Another model for the analysis of biosorption kinetics is pseudo-second-order. The rate law for this system is expressed as

$$t/q_t = (1/k_2 q_e^2) + (t/q_e) \quad (5)$$

where q_t and q_e are the grams of solute sorbed/g biosorbent at any time and at equilibrium, respectively, and k_1 and k_2 are the rate constants of pseudo-first-order sorption and pseudo-second-order sorption, respectively.

Pseudo first order and pseudo second order kinetics models were tested, and the results shows that the pseudo first order obtained the better fit. (Table 3). The rate of biosorption process is shown in Figure 6. The equilibration time showed a fast biosorption rate at the first 15 min of the sorbate-sorbent contact time. This was a larger surface area of the biosorbent which was available for the biosorption of the cadmium ions. This result was in accordance with those extensively reported in the literature[27].

Table 3 Rate constants and equilibrium cadmium ions capacity with $Cd(NO_3)_2.4H_2O$ concentration

pseudo-first order model			pseudo-second order model			This study
k_1	qe (mg/g)	R^2	K^2	qe (mg/g)	R^2	qe (mg/g)
0.79	296.96	0.7922	0.21	12.987	1	12.956

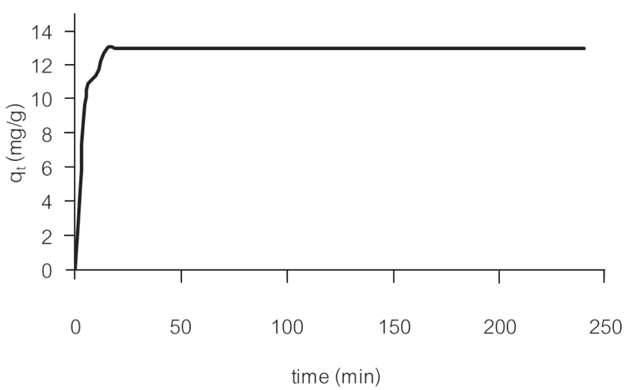

Figure 6 Kinetic of cadmium binding by durian peel

Desorption experiments

Efficient desorption of the cadmium-loaded biosorbent for repeated use is an important attribute for the development of a continuous flow effluent treatment system. Cadmium ions desorption from the durian peel was investigated using solutions of the following three chemicals: 0.3 N HCl, HNO_3 and H_2SO_4 aqueous solution. It can be seen from the results shown in Figure 7 that desorption efficiency using these solutions were 96.58, 89.9 and 85.92%, respectively. The HCl solution is considered as the most promising desorbent.

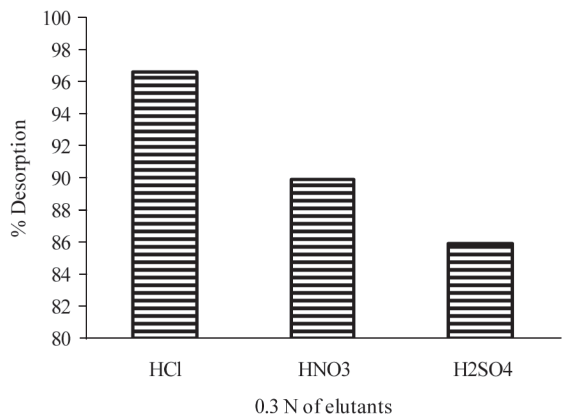

Figure 7 Desorption of cadmium ions from durian peel by using different eluting agents

Characterization of biosorbent

FT-IR spectra before and after biosorption of durian peel are shown in Figures 8 and 9, respectively. FT-IR spectra displayed a number of peaks, indicating the complex nature of the adsorbent. The spectrum displayed the following bands: 3367 (O-H stretching vibrations), 2928 (O-H stretching vibrations), 1741 (C=O stretching vibrations of carboxylic acid), 1621 (C=C stretching vibrations), 1374 (salts of carboxylic acid), 1247, 1057 (C-O-H), 772, 617 and 382 cm^{-1}. The significant shifts of these specific peaks to the higher wave numbers after cadmium ions biosorption suggested that interactions between the cadmium ion and the amide groups occurred on the biomass surface. The band shifted to 3416, indicating that hydroxyl, carboxyl and amide groups were involved in biosorption. The spectra at 1731 cm^{-1} (not shown) became smoother appearance, which would have resulted from the complexion of cadmium ion with the functional groups from proteins. These results indicated that carboxyl, hydroxyl and amide groups on the durian peel surfaces were involved in the biosorption of the cadmium ion.

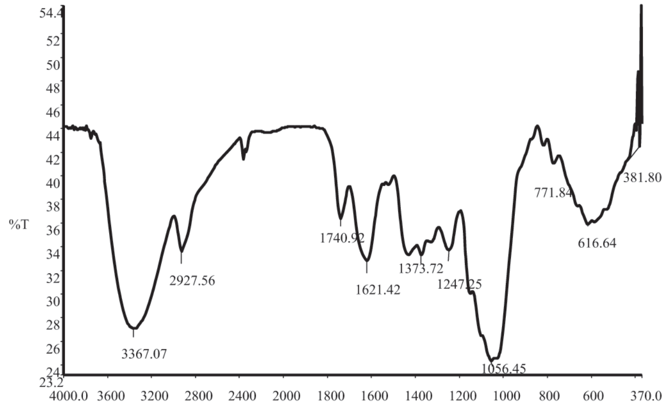

Figure 8 FT-IR spectra of durian peel

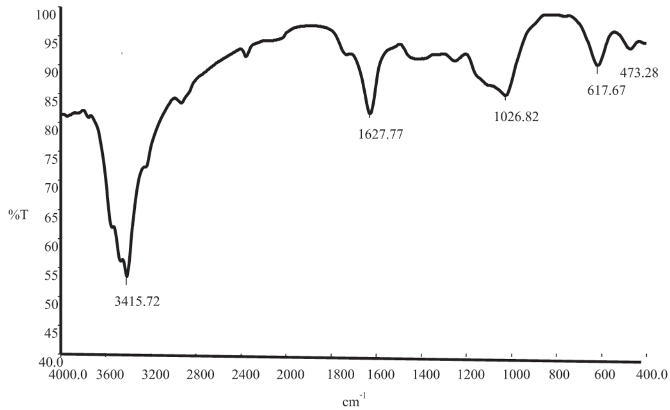

Figure 9 FT-IR of durian peel bound with cadmium ion

The microporous structure of durian peel with particle sizes of 150-212 μm was observed at a resolution of 500x (Figures 10-11). The micrograph of biosorbent shows some cavities in the surface's structure capable of uptaking heavy metal ions as well as an irregular and porous microstructure of the biosorbent. It is clearly seen that there is a considerable modification on morphology of biosorbent before and after cadmium binding.

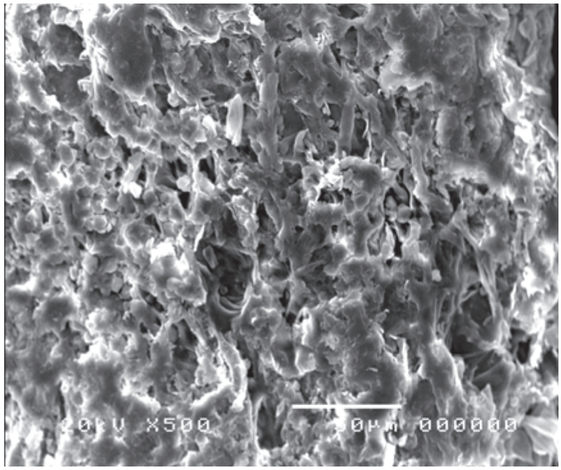

Figure 10 Typical SEM micrograph of durian peel before biosorption of cadmium ions

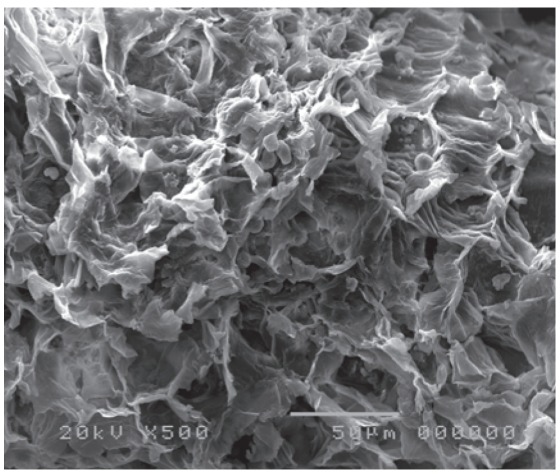

Figure 11 Typical SEM micrograph of durian peel after biosorption of cadmium ions

Conclusion

The durian peel can be used to adsorb cadmium ion from aqueous solution. The potential of durian peel for adsorbing cadmium ions was indicated through its physical and chemical characterization, showing chemical structures (such as COOH, carboxyl, N-H, among others) of this material as well as morphological aspects. The biosorption was dependent on the pH of the solution, agitation speed, temperature, initial cadmium ions concentrations and contact times. The experiment at the equilibrium was fitted well with the Langmuir isotherm model with maximum biosorption capacity of 18.55

mg/g. The biosorption was relatively fast with 15 min after commencing experiment. Biosorption kinetic followed a pseudo-second-order model. The durian peel was a potential candidate for biosorption of cadmium ion and this needs to be further studies for the economical and future use of this biosorbent.

Acknowledgement

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