Adsorption Isotherm of Some Heavy Metals in Water on Unripe and Ripe Peel of Banana

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Received: 28 March 2017; Accepted: 19 June 2017

Abstract

The use of banana peels for removing heavy metals from water was a promising alternative due to the fact that they are abundantly available as agriculture wastes and are available at a low price. In the present study, the potentiality of unripe and ripe banana peels as adsorbents for removing cadmium and lead ions from aqueous solution was investigated by adsorption. The effect of pH, adsorbent dosage, contact time and initial metal concentration were investigated. The experimental result showed that adsorption of cadmium on ripe and unripe banana peels increased with the increase in pH. Maximum uptake took place at pH 3.0 and 5.0 using ripe and unripe banana peels as adsorbent, respectively. The optimum dosage was selected as 30 g/L and the contact time was achieved at 20 minutes for both types of banana peels. For lead adsorption, the maximum adsorption occurred at pH 4.0 and 5.0 with an adsorbent concentration of 40 g/L at 20 minutes using ripe and unripe banana peels as adsorbent. The adsorption phenomenon was fitted with Langmuir isotherm indicated monolayer adsorption. Cadmium uptake capacity was 1.9051 and 2.6185 mg/g using unripe and ripe banana peels, respectively. For lead, the maximum adsorption capacity was 1.630 and 2.8810 mg/g using unripe and ripe banana peels, respectively. Hence, ripe banana peels have greater potential than unripe banana peels for both types of metal ions adsorption. The removal of lead had a higher adsorption capacity than cadmium.

Keywords: Adsorption, Banana peel, Heavy metals, Cadmium, Lead

Introduction

Heavy metal contamination has become a global environmental concern, mainly due to the fact that heavy metals are non-biodegradable substances with a long biological half-life. Heavy metals exhibit harmful effects in living organisms and can affect the human through the food chain (Fu & Wang, 2011; Khanna, 2011). Cadmium and lead are heavy metals that are widely used in industrial activities such as mining, and the manufacture of batteries, pigments and plastics. They have been classified by the United States Environmental Protection Agency (USEPA) as a probable human carcinogen. Exposure to cadmium disrupts the function of vital organs, such as the lungs and the kidneys. Furthermore, long-term exposure to low levels of cadmium results in osteoporosis and osteomalacia. Lead exposure is generally associated with the damage to erythropoietic, neural, renal and hepatic systems. Thus, the eradication of these heavy metals from wastewater is necessary in order to protect living organisms in the ecological system (Agency for Toxic Substances and Disease Registry, 2007; Agency for Toxic Substances and Disease Registry, 2012; Fu, & Wang, 2011; Tchounwou, Yedjou, Patlolla, & Sutton, 2012; United States Environmental Protection Agency, 2017).

Numerous approaches have been developed and introduced to water purification, for instance, precipitation, coagulation (Charerntanyarak, 1999; Tang et al., 2016), reverse osmosis (Bakalár, Búgel, & Gajdošová, 2009), ion exchange (Bai & Bartkiewicz, 2009) photocatalysis (Chowdhury, Elkamel, & Ray, 2015), solvent extraction (Cerna, 1995), membrane filtration, electrodialysis and electrochemical methods. Nevertheless, there are some obvious disadvantages associated with the usage of all previously mentioned methods, such as their high cost, large chemical consumption, generation of toxic sludge and non-regenerative ability. Consequently, a growing interest in adsorption has been observed in order to eliminate heavy metals in wastewater instead of conventional methods because it is inexpensive, highly efficient and capable of regeneration (Nguyen et al., 2013).

In recent years, the characteristics of agricultural waste and by-products as adsorbents have been extensively investigated for wastewater treatment. (Bhatnagar, Sillanpää, & Witek-Krowiak, 2015; De Gisi, Lofrano, Grassi, & Notarnicola, 2016; Nguyen et al., 2013). Despite the increasing amount of research regarding these adsorbents, the comparative study of the adsorption capacity of unripe and ripe agricultural waste peels as adsorbent has not been dealt with in depth.

In the Bangkrathum district, Phitsanulok, Thailand, there are many banana processing factories, and consequently, a large availability of waste associated with bananas, especially banana peels causing waste disposal problems. Therefore, the utilization of banana peels as adsorbent was considered for sequestering heavy metals in wastewater.

The purpose of this study was to assess and compare the potentiality of unripe and ripe banana peels as adsorbent for the adsorption of cadmium and lead ions from aqueous solution. The effects of pH, adsorbent dosage, contact time and initial metal concentration were evaluated. Adsorption isotherm was investigated to elucidate adsorption phenomena.

Methods and Materials

Chemicals

Cadmium nitrate and lead nitrate were purchased from Ajax Finechem Pty Limited, Australia. Hydrocholic acid (HCl) 37% was procured from RCI Labscan Limited, Thailand. Sodium hydroxide (NaOH) was obtained from Ajax Finechem Pty Limited, Australia. All previous mentioned chemicals were analytical grade. Cadmium and lead AAS standard solution 1000 mg/L were the products of Loba Chemie Pvt. Ltd., India.

Equipment

pH adjustment was performed using HCl (1 M) and NaOH (1 M) (Seven Easy, Mettler-Toledo International Inc., USA). Analysis of metal ions concentration was conducted by flame atomic absorption spectroscopy (FAAS) (AAnalyst 200, PerkinElmer, Inc., USA). The absorbance of cadmium and lead ions was recorded at 228.80 and 283.31 nm, respectively.

Preparation of adsorbent

The first step is that bananas (*Musa sapientum* Linn) were collected from the Bangkrathum district, Phitsanulok, Thailand. Next, the unripe and ripe banana peels were separated from the fruits, washed with tap water followed by deionized water. Then, they were dried by sunlight for 5 days and placed in a hot air oven at 70°C for 3 hours. After dehydration, banana peels were digested by cutting and grinding and then sifted through a 60-mesh sieve. Lastly, the sample was stored in a desiccator for further usage.

Preparation of metal ion in aqueous solution

The stock solutions of cadmium and lead ions (1000 µg/mL) were prepared by dissolving required amount of cadmium nitrate and lead nitrate in deionized water. After that, cadmium and lead ions solutions were prepared by diluting the stock solution with deionized water to the desired concentration.

Adsorption studies

The experiments were carried out in triplicate for each sample using the batch system. The concerned parameters, including pH, adsorbent dosage, contact time and initial concentration were assessed as follows:

1. Effect of pH

To investigate the optimum pH value, first of all, 50 µg/mL of cadmium and lead ions solution (50 mL) were adjusted pH value ranging from 2.0 to 8.0

using HCl (1 M) and NaOH (1 M). Next, 40 g/L of adsorbent dosage were added into the solution. Then, the sample was agitated at 100 rpm for 20 minutes. After agitation, the suspension was passed through filter paper. Finally, the residual metal ions concentration was determined using FAAS. The absorbance of cadmium and lead ions was recorded at 228.80 and 283.31 nm, respectively.

2. Effect of adsorbent dosage

To identify the optimum adsorbent dosage, in the beginning, the pH value of 50 µg/mL of metal ions solution (50 mL) was adjusted by the result obtained from section 3.1. Next, the adsorbent dosage was varied from 10 to 60 g/L. Following this, the sample was agitated at 100 rpm for 20 minutes. Then, the suspension was passed through filter paper. Lastly, the supernatant was analyzed for metal ions concentration using FAAS.

3. Effect of contact time

To assess the optimum contact time, firstly, cadmium and lead ions solution (50 mL) were adjusted pH value and used adsorbent dosage by the result obtained from section 3.1 and 3.2, respectively. Secondly, the sample was agitated at 100 rpm by varying the contact time from 2 to 60 minutes. Thirdly, the suspension was passed through filter paper. Finally, the concentration of residual metal ions was determined using FAAS.

4. Effect of initial concentration

To determine the effect of initial concentration, the first step is that the concentration of 30 to 80 µg/mL of cadmium and lead ions solution (50 mL) was dissolved from stock solution to get the desired concentrations. Next, the optimum pH, adsorbent dosage and contact time were adjusted by the result obtained from section 3.1, 3.2 and 3.3, respectively. After that, the sample was then agitated at 100 rpm. In addition, the suspension was passed through the filter paper. Lastly, the residual metal ions concentration was measured using FAAS.

Data analysis

The adsorption quantity and adsorption yield were calculated using the following equations:

$$q = (C_0 - C)/R \tag{1}$$

$$\%\ \text{adsorption} = ((C_0 - C)/C_0)*100 \tag{2}$$

where q (mg/g) is the quantity of metal ions adsorbed per unit mass of adsorbent, C_0 (mg/L) is the initial metal ions concentration, C (mg/L) is the metal ions concentration after adsorption and R (g/L) is the mass of adsorbent per liter of aqueous solution.

Langmuir and Freundlich isotherm were calculated using these following equations:

$$C_e/q_e = 1/bq_m + C_e/q_m \tag{3}$$

$$\text{Log } q_e = \log K_F + ((1/n)(\log C_e)) \tag{4}$$

where C_e and q_e are the equilibrium metal ion concentration in solutions (mg/L) and on adsorbents, respectively, b (L/g) is Langmuir isotherm parameters, q_m is the maximum adsorption capacity (mg/g), K_F ($mg^{1-1/n}$ g^{-1} $L^{1/n}$) is the Freundlich constant and 1/n is heterogeneity factor related to adsorption intensity.

Results and Discussion

Effect of pH

pH is recognized as a major factor influencing to the adsorption process. The study was carried out by varying pH from 2 to 8. The obtained results showed that cadmium adsorption yield increased from 73.29% to 77.75% and 29.69% to 43.43% when the pH solution increased from 2.0 to 3.0 and 2.0 to 5.0 using ripe and unripe banana peels, respectively (Figure 1, 2). For lead adsorption, it can be seen that the percentage removal increased from 93.15% to 98.52% and 84.97% to 92.86% with the rise in pH from 2.0 to 4.0 and 2.0 to 5.0 using ripe and unripe banana peels, respectively (Figure 3). Therefore, the optimum pH was observed at pH 3.0 and 5.0 for cadmium, as well as pH 4.0 and 5.0 for lead using ripe and unripe banana peels. Beyond the optimum pH, the adsorption yield decreased for both types of metal ions. This behavior could be explained by the precipitation as metal hydroxide (Anwar et al., 2010). These results indicated that at the lower pH value, metal ions competed with H^+ to attach the adsorbent surfaces, leading to the increasing of adsorption yield. As pH increased, the removal percentage increased as well. This trend could be attributed by the elevation of negative charged site. Similar tendencies were reported by Barka et al., 2013. for the case of removing cadmium and lead by dried cactus (*Opuntia ficus indica*) cladodes.

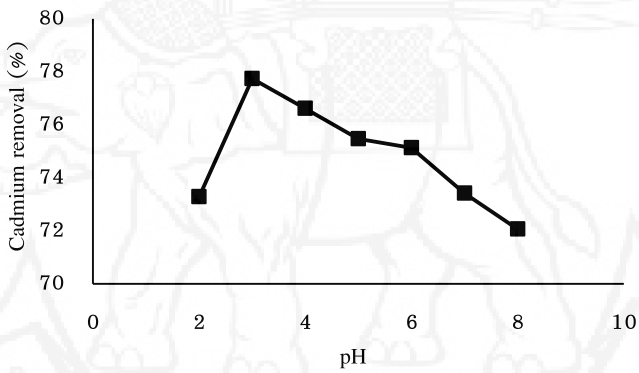

Figure 1 Effect of pH of cadmium removal using ripe banana peel (metal concentration = 50 µg/ml, adsorbent dose = 40 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

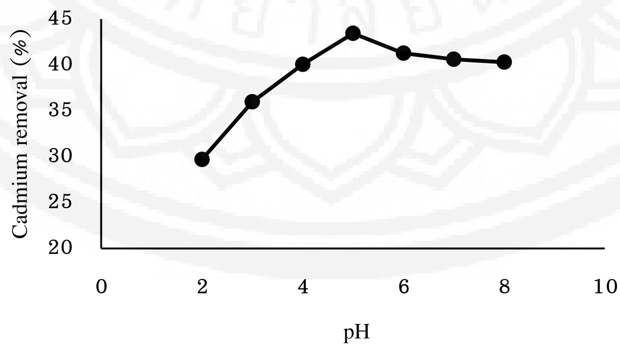

Figure 2 Effect of pH of cadmium removal using unripe banana peel (metal concentration = 50 µg/ml, adsorbent dose = 40 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

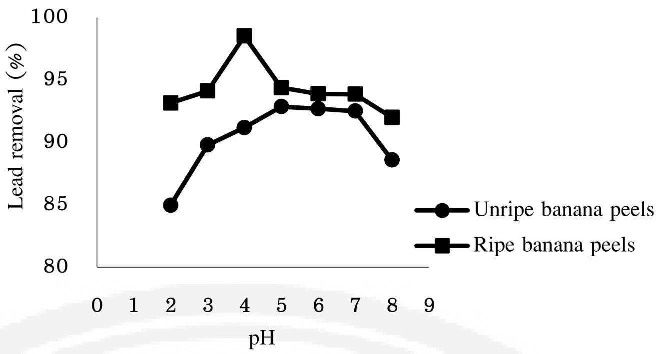

Figure 3 Effect of pH of lead removal (metal concentration = 50 μg/ml, adsorbent dose = 40 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

Effect of adsorbent dosage

The adsorbent dosage study was performed by varying 10-60 g/L of ripe and unripe banana peel. We explored that the maximum removal of cadmium was 47.52% and 79.02% at the concentration of 30 g/L for both unripe and ripe banana peels, respectively (Figure 4). The adsorption of lead was 91.26% and 99.19% by using 40 g/L of unripe and ripe banana peels, respectively (Figure 5). This behavior indicated the more available surface area with the rise in adsorbent dosage (Anwar et al., 2010; Barka et al., 2011; Karthikeyan et al., 2007). However, at higher adsorbent concentration, the removal of metal ions decreased due to overlapping and partial aggregation (Boota et al., 2009).

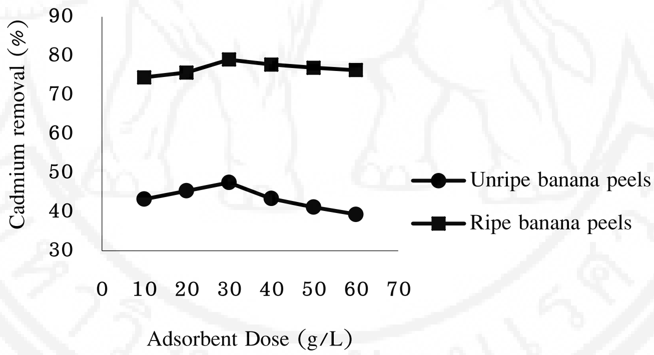

Figure 4 Effect of adsorbent dose of cadmium removal (metal concentration = 50 μg/ml, pH = 3.0 and 5.0 for ripe and unripe banana peels, respectively, adsorbent dose = 10-60 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

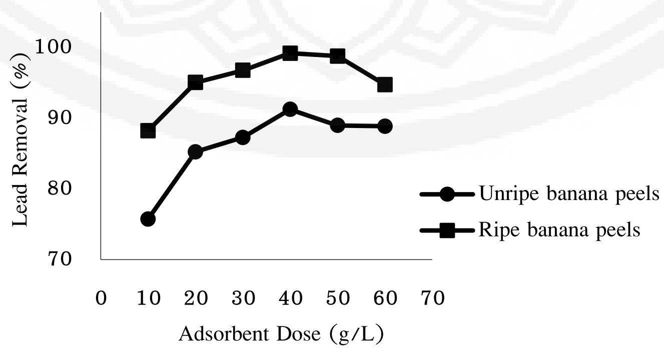

Figure 5 Effect of adsorbent dose of lead removal (metal concentration = 50 μg/ml, pH = 4.0 and 5.0 for ripe and unripe banana peels, respectively, adsorbent dose = 10-60 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

Effect of contact time

The contact time between adsorbates and adsorbents were carried out by varying from 2 to 60 minute to assess the optimum contact time that the process reaching equilibrium. The results were presented in Figure 6 and 7. They illustrated that the metal removal increased rapidly within 10 minute with the increased in contact time and reached equilibrium at 20 minutes.

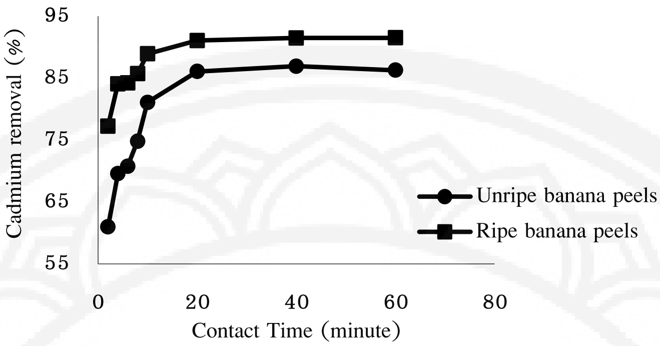

Figure 6 Effect of contact time of cadmium removal (metal concentration = 50 µg/ml, pH = 3.0 and 5.0 for ripe and unripe banana peels, respectively, adsorbent dose = 30 g/L, contact time = 2-60 minutes, agitation speed = 100 rpm, temperature = 25 °C)

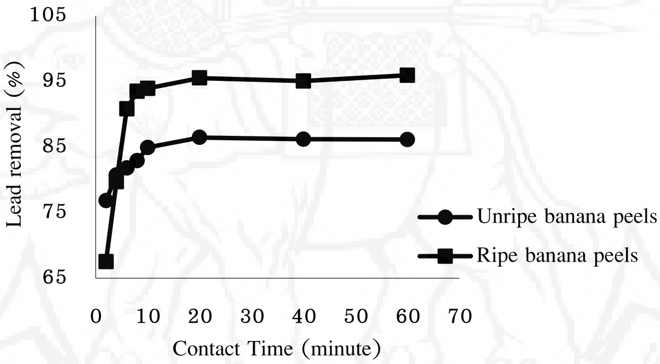

Figure 7 Effect of contact time of lead removal (metal concentration = 50 µg/ml, pH = 4.0 and 5.0 for ripe and unripe banana peels, respectively, adsorbent dose = 40 g/L, contact time = 2-60 minutes, agitation speed = 100 rpm, temperature = 25 °C)

Effect of initial concentrations

The initial concentrations were carried out by varying 30-60 µg/ml of metal ions in the solution. The obtained results showed that the adsorption capacity increased with the increase in the initial solutions. This trend may be informed that the metal ions were adsorbed continuously on the surface of adsorbents (Figure 8, 10) by the high driving force between adsorbates and adsorbents. However, the percent of metal removal decreased because of the limitation of binding sites (Malkoc & Nuhoglu, 2005). (Figure 9, 11)

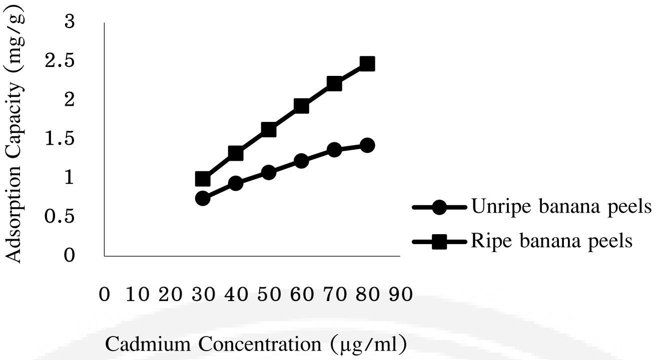

Figure 8 Effect of initial concentration of cadmium adsorption capacity (metal concentration = 30-80 µg/ml, pH = 3.0 and 5.0 for ripe and unripe banana peels, respectively, adsorbent dose = 30 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

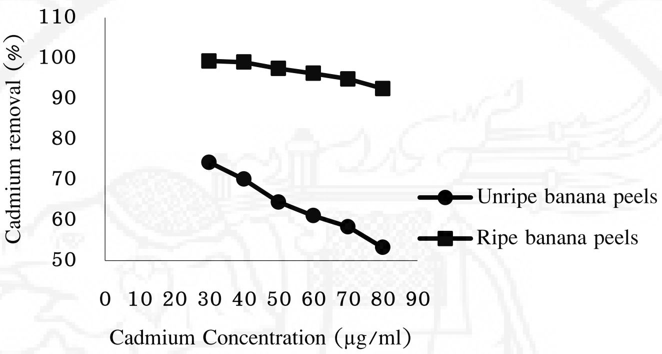

Figure 9 Effect of initial concentration of cadmium removal (metal concentration = 30-80 µg/ml, pH = 3.0 and 5.0 for ripe and unripe banana peels, respectively, adsorbent dose = 30 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

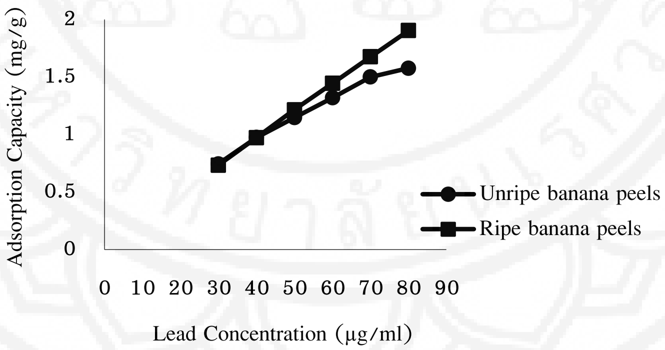

Figure 10 Effect of initial concentration of lead adsorption capacity (metal concentration = 30-80 µg/ml, pH = 4.0 and 5.0 for ripe and unripe banana peels, respectively, adsorbent dose = 40 g/L, contact time = 20 minutes, agitation speed = 100 rpm,
temperature = 25 °C)

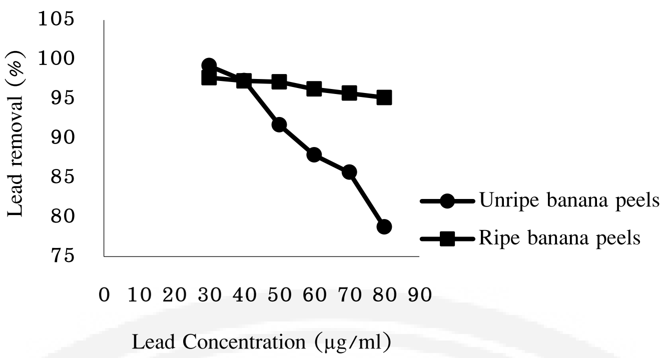

Figure 11 Effect of initial concentration of lead removal (metal concentration = 30-80 µg/ml, pH = 4.0 and 5.0 for ripe and unripe banana peels, respectively, adsorbent dose = 40 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

Adsorption Isotherm Study

The Langmuir and Freundlich isotherms were calculated by equation (3) and (4), respectively, to attribute the adsorption phenomenon of cadmium and lead ions solution on ripe and unripe banana peels. As shown in table 1 and 2, we explored that Langmuir isotherm was suitable for this study comparing with Freundlich isotherm with the value of R^2 close to 1 (Figure 12-19). Cadmium maximum uptake was 1.9051 and 2.6185 mg/g for unripe and ripe banana peels, respectively. Lead adsorption capacity was 1.6300 and 2.8810 mg/g for unripe and ripe banana peels, respectively. Thus, the adsorption of cadmium and lead was a monolayer adsorption. The maximum capacity was quite low comparing with other adsorbents (Table 3). Nevertheless, the findings of the current study do not support the previous research published by Anwar et al. (2010). They investigated that cadmium had higher adsorption capacity than lead using banana peel as adsorbent. They attributed this effect to the difference of size of these metal ions. Cadmium has smaller size than lead, and consequently, it exhibited high metal uptake comparing with lead.

Table 1 Langmuir isotherm parameters

Metal	Adsorbent	R^2	q_m (mg/g)	b (L/g)
Cadmium	Unripe banana peels	0.9954	1.9051	0.0795
	Ripe banana peels	0.9905	2.6185	1.8125
Lead	Unripe banana peels	0.9907	1.6300	1.0079
	Ripe banana peels	0.9915	2.8810	0.4777

Table 2 Freundlich isotherm parameters

Metal	Adsorbent	R^2	n	K_F ($mg^{1-1/n} g^{-1} L^{1/n}$)
Cadmium	Unripe banana peels	0.9895	2.3878	0.3233
	Ripe banana peels	0.9851	3.8850	1.5704
Lead	Unripe banana peels	0.9823	5.6561	0.9473
	Ripe banana peels	0.9875	1.8298	0.9273

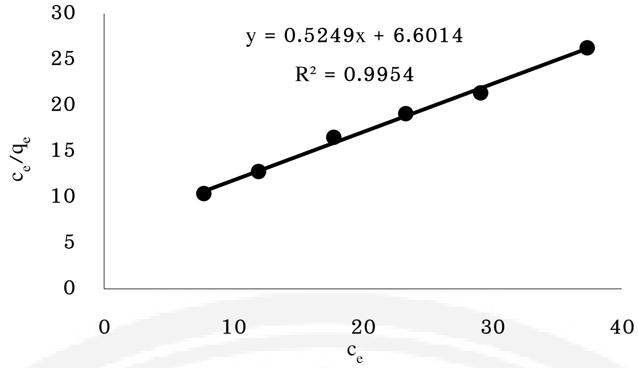

Figure 12 Langmuir isotherm for cadmium adsorption using unripe banana peels (metal concentration = 30-80 μg/ml, pH = 5.0, adsorbent dose = 30 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

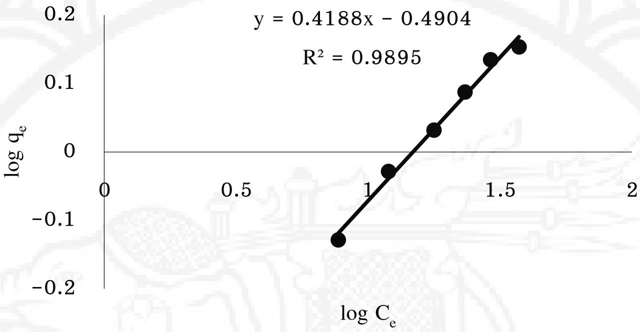

Figure 13 Freundlich isotherm for cadmium adsorption using unripe banana peels (metal concentration = 30-80 μg/ml, pH 5.0, adsorbent dose = 30 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

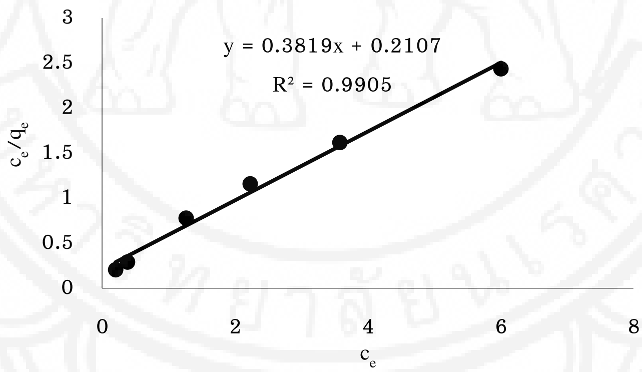

Figure 14 Langmuir isotherm for cadmium adsorption using ripe banana peels (metal concentration = 30-80 μg/ml, pH = 3.0, adsorbent dose = 30 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

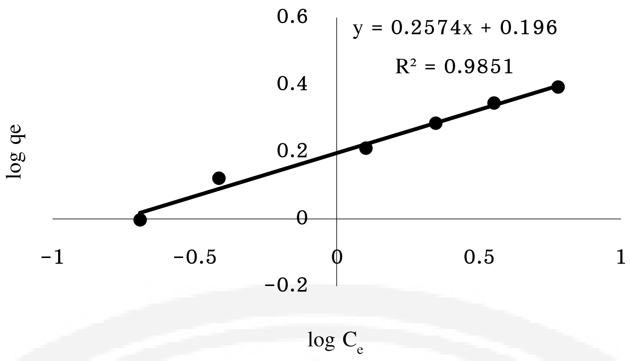

Figure 15 Freundlich isotherm for cadmium adsorption using ripe banana peels (metal concentration = 30-80 µg/ml, pH = 3.0, adsorbent dose = 30 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

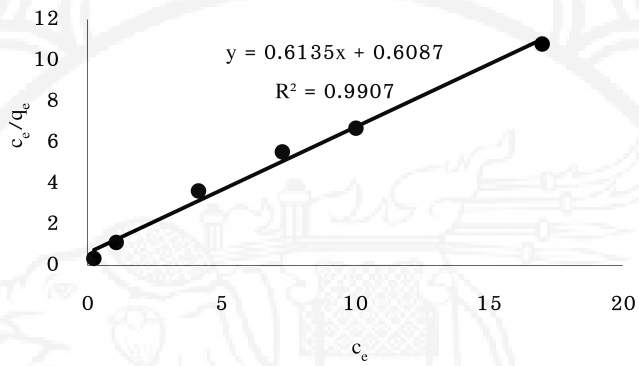

Figure 16 Langmuir isotherm for lead adsorption using unripe banana peels (metal concentration = 30-80 µg/ml, pH = 5.0, adsorbent dose = 40 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

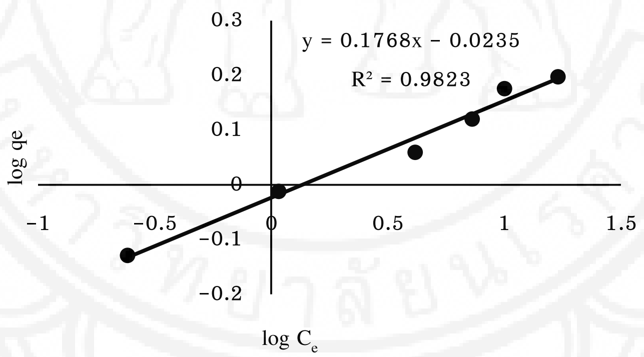

Figure 17 Freundlich isotherm for lead adsorption using unripe banana peels (metal concentration = 30-80 µg/ml, pH = 5.0, adsorbent dose = 40 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

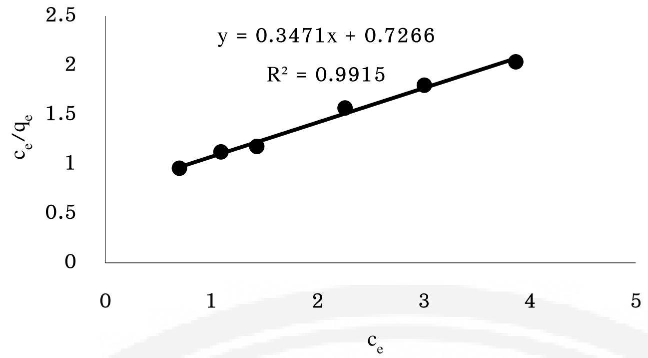

Figure 18 Langmuir isotherm for lead adsorption using ripe banana peels (metal concentration = 30-80 μg/ml, pH = 4.0, adsorbent dose = 40 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

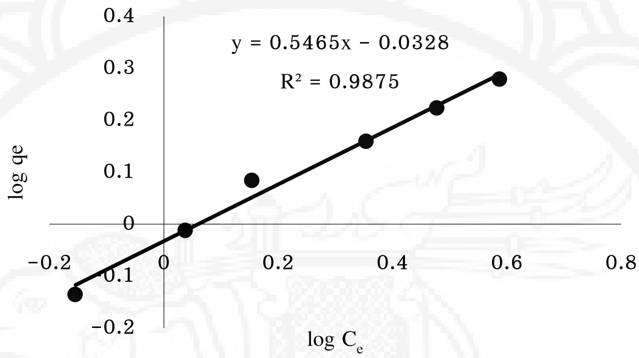

Figure 19 Freundlich isotherm for lead adsorption using ripe banana peels (metal concentration = 30-80 μg/ml, pH = 4.0, adsorbent dose = 40 g/L, contact time = 20 minutes, agitation speed = 100 rpm, temperature = 25 °C)

Table 3 Comparison of maximum adsorption capacity of unripe and ripe banana peels for cadmium and lead with different adsorbents

Adsorbent	qm (mg/g) cadmium	qm (mg/g) lead	References
Banana peels	5.71	2.18	Anwar et al., 2010
Cactus cladodes	30.42	98.62	Barka et al., 2013
Oyster mushroom (*Pleurotus platypus*)	34.96	27.10	Vimala & Das, 2009
Alhaji maurorum seed	3.75	-	Ebrahimi et al., 2015
Lentil husk	107.31	-	Basu et al., 2017
Grapefruit peel	42.09	-	Torab-Mostaedi et al., 2013
Coffee grounds	15.65	-	Azouaou et al., 2005
Rogers mushroom (*Lepiota hystrix*)	-	3.8	Kariuki et al., 2017
Taro (*Colocasiaesculenta*(L.) Schott)	-	291.56	Saha et al., 2017
Lentil husk	-	81.43	Basu et al., 2015
Ponkan peel	-	112.1	Pavan et al., 2008
Unripe banana peels	1.9051	1.6300	This study
Ripe banana peels	2.6185	2.8810	This study

Conclusion

In the present study, the efficacy of unripe and ripe banana peels as an adsorbent for removing cadmium and lead ions from aqueous solution was investigated by adsorption. The results obtained showed that the increase of pH, adsorbent dosage, contact time and initial concentration were capable of rising both metal ions uptake. The adsorption phenomenon was suitable with Langmuir isotherm denotes monolayer adsorption.

Ripe banana peels had more potential than unripe banana peels for both types of metal ions adsorption. The removal of lead had higher adsorption capacity than cadmium. Thus, ripe banana peels is the promising low cost adsorbents in the case of adsorption of cadmium and lead ions from aqueous solution. It is recommended that further research should be undertaken in the other process parameters influencing the adsorption process such as temperature and agitation speed in order to improve adsorption efficiency. Binary or tertiary of metal ions in aqueous solutions should be studied because wastewater is often contaminated with several heavy metals, rather than just one. Moreover, pretreatment of the adsorbent is necessary in order to modify the functional groups of adsorbent to reach the highest adsorption capacity. In addition, using eluent in order to desorb the adsorbent is useful in the recovery of adsorbates for reuse.

Acknowledgement

Authors are thankful to Naresuan University for financial support.

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