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Removal of Lead(II) from Aqueous Solution Using Fibroin from Cocoon Waste as a Potential Biosorbent

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ABSTRACT

The effective removal of heavy metals from aqueous wastes is an important issue for many industrialized countries. In this study, removal of Pb(II) from aqueous solutions was studied using fibroin from two cocoon silk species: TxC Cocoon (TxC) and Lueang Surin Cocoon (LSC). The effect of various operational parameters i.e., adsorbent dosage, pH, contact time and solute concentration was investigated. The results, LSC showed higher adsorption efficiency of Pb(II) metal than TxC in all the parameters, possibly because LSC contained higher fibroin content. The optimum set of conditions for adsorption of Pb(II) ion was found to be adsorbent dosage 0.25 g, pH 6, contact time 100 min and initial concentration 50 mg/L, obeyed pseudo second order kinetic model. The adsorption data conformed to both the Langmuir and the Freundlich isotherms, but fitted best into the Langmuir model. The R^2 values for Langmuir equation were 0.9997 and 0.9996 for TxC and LSC, respectively. The Langmuir monolayer adsorption capacity values of the cocoons were calculated to be 51.813 mg/g and 52.352 mg/g for TxC and LSC, respectively. The results indicated that the fibroin from both cocoon wastes can be used to effectively adsorb Pb(II) ions as low-cost biosorbents from wastewater treatment plants.

Keywords: Adsorption capacity; Biosorption; Lead(II); Fibroin; Cocoon waste

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1. Introduction

Water is one of the important environmental compartments for living organisms. Nowadays, it is found that humans use water regardless of its importance. After using water to purify the body and utensils, it is released as wastewater into rivers without filtering or treating, causing water pollution. Wastewater contains undesirable substances or sewage probably including contaminated heavy metals. Heavy metals are commonly found contaminating wastewater, e.g., lead (Pb), cadmium (Cd) and chromium (Cr), which are used as components for the production of batteries, electrical equipment, alloys and automobile parts, as well as in the mining and dyeing industries. These industries can contaminate water sources with residual heavy metals. Particularly, lead pollutants occur in many countries around the world because lead is a substance that is stable, does not decompose naturally, can be found in both organic and inorganic compounds, and has high toxicity. Lead can enter the human body in three ways comprising eating, respiration and skin. If it is accumulated in large amounts or through long exposure, chronic effects may occur in both humans and animals by directly affecting the blood and brain disorders (especially in young children), nephropathy, colic–like abdominal pains and miscarriage [1-3].

Heavy metal contamination in the environment has increased sharply since the beginning of the 20th century, as a result of the industrial revolution and excessive population growth, posing major environmental and human health problems worldwide [4]. It is alarming both in developed and developing countries, and a critical issue threatening ecology [5]. Several contaminated sources include emissions from waste incinerators, car exhaustions, organic and inorganic industries, and agricultural amendments such as sludge or composts, pesticides and mineral fertilizers. The degree of contamination of the waters depends on time and activities,

contributing to contaminated areas. Then, it is obviously important to remove these toxic metals from these contaminated areas in order to control the hazardous effects, owning to spreading and leaching to nearby agricultural soil and groundwater. Nowadays, there are various methods for treating heavy metals from water sources, such as chemical precipitation and sedimentation, electrochemical treatment, activated carbon, and biological treatment. However, some methods have limitations in therapy and there are many problems in treatments. For example, the chemical precipitation method and the electrochemical process have the limitation on the concentration of heavy metals which cannot be treated in the range of 1-100 mg/L and biological treatment by using microorganisms as adsorbents has also encountered problems such as the inability to separate heavy metals from microorganisms, etc. Adsorption is one of the most popular methods that many researchers have been interested in and have tried to develop low-cost sorbents to replace expensive sorbents for increasing the efficiency of treatment. Moreover, the application of natural materials as biosorbents is increasingly used to adsorb heavy metals in wastewater [6].

Therefore, the present study investigated the possibility of Pb(II) adsorption material with two species of cocoon wastes: TxC Cocoon (TxC) and Lueang Surin Cocoon (LSC) as potential biosorbents, which are highly effective in treating and are safe for humans as green materials. The physical characteristics of the two cocoon wastes have different shades; with TxC the cocoon is white, while the unique LSC of Surin province has the characteristic yellow cocoon. In addition, the idea of using cocoons to treat Pb(II) contaminated in wastewater is considered to reduce the cost of wastewater treatment and to use by-product materials as another benefit similar to other biosorbents such as activated carbon and fruit shells. It is hoped that knowledge gained from this

research will be important information for the development of biosorbents and suitable for the application of adsorbing other heavy metals in wastewater.

2. Materials and Methods
2.1 Preparation of adsorbents

Two species of cocoons, the TxC and LSC, were cut to about 5x5 mm. Then, the silk glue was stripped using 0.6 M Na-HCO$_3$ solution at a volume of 100 mL per 1 g of the cocoon, boiled at 80 ^{o}C for 40 min and filtered with filter paper for obtaining cocoons. After that, the cocoons were soaked in HNO$_3$ acid at concentration 0.1 M for 3 h and washed with 2-3 times deionized (dI) water and kept at room temperature for 24 h. Finally, they were packed in a zipper bag and then stored in a desiccator for adsorption studies.

2.2 Preparation of wastewater sample

All reagents used for this study were analytical reagent grade. The 1,000 mg/L aqueous solutions of the metal ions were prepared as stock from Pb(NO$_3$)$_2$ in a 1-liter volumetric flask, adjusted the volume with dI water to receive 1,000 mg/L Pb(II) synthetic wastewater. From the stock, working solutions of different concentrations were prepared from appropriate aliquots diluted to the appropriate concentrations. The total concentration of each metal ion in the aqueous solution was confirmed by analysis using Atomic Adsorption Spectrometer (AAS) (PerkinElmer Analyst 400).

2.3 Experimental procedures

Adsorption experiments were carried out to study the effect of adsorbent dosage, pH, contact time and solute concentration on the adsorption of Pb(II) of cocoons. The experiments were carried out using 50 mL of lead(II) metal solution of the initial concentration of 50 mg/L, pH 6, and 0.25 g of the adsorbents. At the end of each experiment, the contents of each tube were filtered using filter paper in which concentrations of residual metal ions in each filtrate were determined. All experiments were carefully conducted to acquire the best result.

2.4 Batch adsorption studies

Each of the batch adsorption studies was carried out by contacting the cocoon adsorbents with the metal ions in a 50 mL stopper conical flask. The experiments were conducted at 30°C to determine the effects of pH, adsorbent dosage, contact time, and initial ions concentration on the biosorption of Pb(II) ions. Each experiment was conducted in a mechanical shaker. The samples were filtered through Whatman filter paper and the metal ion concentration was determined in the filtrate. To distinguish between possible metal precipitation and actual metal sorption, controls (blank) were used without adsorbent materials.

The remaining concentration of Pb(II) after adsorption was measured using AAS and the amount of adsorption at equilibrium, q_e (mg/g) was calculated by equation (2.1):

$$q_e = \frac{(C_o - C_e)}{W} \times V, \qquad (2.1)$$

where C_o and C_e (mg/L) are the liquid-phase concentrations of lead at initial and equilibrium, respectively, V is the volume of solution (L) and W is the mass of dry adsorbent (g) used. The percentage of removal of Pb(II) can be calculated as equation (2.2):

$$\%Removal = \frac{(C_o - C_e)}{C_o} \times 100. \qquad (2.2)$$

2.5 Variation of adsorbent dosage

The adsorption of the metal ions on cocoons was studied at various weights: 0.10, 0.25 and 0.50 g. The sorption studies were carried out using 50 mL of lead(II) solution of an initial concentration of 50 mg/L. The metal ion solutions were measured into three labeled beakers, each containing 0.10, 0.25 and 0.50 g of the adsor-

bents and uniformly agitated at 30°C for 30 min many times. The experiment was a solution setup at pH 6. After agitation, the content of each beaker was filtered and the residual concentrations of metal ions in the filtrates were determined using AAS and the amount of metal ions adsorbed was calculated.

2.6 Variation of pH

The adsorption of the metal ions on cocoons was studied at various pH 3, 5, 6 and 7. The sorption studies were carried out using 50 mL of Pb(II) solution of an initial concentration of 50 mg/L. The metal ion solutions were measured into three labeled beakers, each containing 0.25 and 0.50 g of biosorbents and uniformly agitated at 30°C for 30 min many times. At the end of each pH analysis, the content of each tube was centrifuged and filtered. The concentrations of metal ions in the filtrates were determined using AAS, and the amount of metal ions adsorbed was calculated.

2.7 Variation of contact time

The adsorption of the metal ions on cocoons was studied at various time intervals: 15, 30, 60 and 100 min. The sorption studies were carried out using 50 mL of lead(II) solution with an initial concentration of 50 mg/L. The metal ion solutions were measured into three labeled beakers each containing 0.25 g of the adsorbent and uniformly agitated at 30°C for 15 min. The experimental setup was repeated for various time intervals of 15, 30, 60 and 100 min many times. At the end of each contact time, the content of each tube was centrifuged and filtered. The concentrations of metal ions in the filtrates were determined using AAS and the amount of metal ions adsorbed was calculated.

2.8 Variation of solute concentration

The adsorption was carried out using initial lead(II) ion concentrations of 50, 100, 150 and 250 mg/L for an aqueous solution of Pb(II). The 0.25 g of each cocoon adsorbent was weighed into each of the three beakers and 50 mL of 50 mg/L of Pb(II) solution was measured into beakers and uniformly agitated with the use of a platform shaker at a fixed temperature of 30°C for 30 min, after which the content of each beaker was filtered into clean sample bottles. HCl or NaOH solutions were used to adjust the pH 6 condition. The concentrations of residual metal ions in the filtrates were determined using AAS. The amount of metal ions adsorbed from the solution was determined by difference.

2.9 Characterization of cocoons adsorbent

The characterization of fibroin is the main component found in the cocoons by Fourier-transform infrared spectrometer (FT-IR: Shimudsu FTIR-8900) in the wavenumber ranging from 4000-450 cm^{-1}. The FT-IR technique is an important tool to identify the characteristics of functional groups, which are instrumental in the adsorption of metal ions.

3. Results and Discussion
3.1 Characteristics of biosorbents

The characterization of fibroin is the main component found in the cocoons by FT-IR technique. The FT-IR spectra of TxC before and after Pb^{2+} ion biosorption process are shown in Fig. 1. The results show that the silk cocoons have different functional groups such as amide, serine amino acid, lysine amino acid and coil structure. Some of these functional groups were changed after the biosorption process. The comparison of the FT-IR spectra of the cocoons and after Pb^{2+} biosorption illustrated the following bands and peaks. The adsorption bands around 3500-3309 cm^{-1} are the N-H stretching vibrations of serine amino acid. The small peak located at 2958 cm^{-1} is the stretching characteristics of -CH of aromatic compounds. The additional peaks located at 1675, 1542 and 1229 cm^{-1} indicate amide I,

amide II and amide III, respectively. The lysine amino acid group vibration at 1164 cm^{-1} may be attributed to the deformation vibration of N-H bending of amino groups. The peaks at 1239 and 669 cm^{-1} are possibly due to the coil structure. Interestingly, the after-adsorption peaks of cocoons are shifted pronouncedly by ≈30 cm^{-1}, indicating that Pb^{2+} ions can adsorb to the N-H position of the fibroin as shown in the spectrum 1B. For this reason, the shift of these peaks is due to the influence of Pb^{2+} adsorbed with the active N-H group within the structure of the fibroin of the cocoons themselves [7-8].
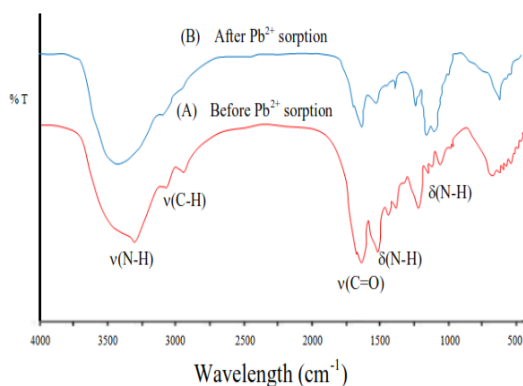

Fig. 1. Comparison the FT-IR spectra of TxC (A) before and (B) after Pb^{2+} adsorption.

3.2 Effect of adsorption efficiency

As seen in Table 1, both species of cocoon adsorbents showed very similar adsorption performance. The products obtained were characterized and utilized for the removal of Pb(II) from aqueous solutions over a wide range of adsorbent dose (0.01-0.50 g), pH (3-7), contact time (15-100 min) and initial metal ion concentration (50-250 mg/L). The optimum set of conditions for biosorption of Pb(II) ion was found to be dosage 0.25 g, pH 6, contact time 100 min and initial concentration 50 mg/L.

Furthermore, the amino group of fibroin at the active site can adsorb Pb^{2+} ions very well. Therefore, the cocoons have more metal-binding active sites and more negative surface, which enhances the retention of Pb^{2+} onto the surface. Thus, it showed the highest removal of Pb(II). However, the adsorption mechanism of metal ions depends on various factors such as pH of the solution and binding characteristics. Usually, metal ion adsorption is accomplished by ion exchange, complex formation, electrostatic interaction and precipitation. In the present study, Pb(II) adsorption is explained by pH effect and characterization techniques by FT-IR, which supported the binding of Pb^{2+} on cocoon. These groups electrostatically interact with Pb^{2+} and Pb(OH)$_2$ [9] and at higher pH lead hydroxides get precipitated on the surface of cocoon adsorbent as illustrated in Fig. 2.

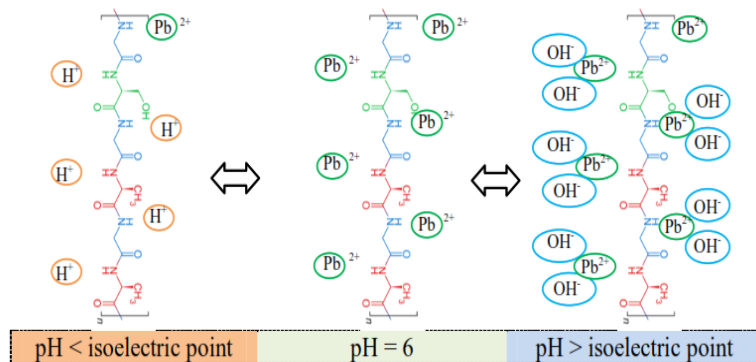**Fig. 2.** Schematic mechanism of Pb(II) interaction with cocoon adsorbent.

Table 1. Comparison of adsorption efficiency and percentage of removal of Pb(II) on cocoons as effects of various operational parameters.
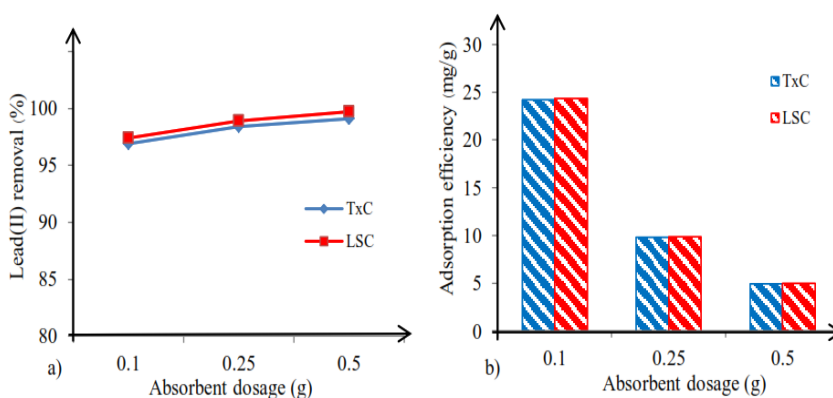
Effect	Condition		Pb(II) removal (%)*	
			TxC	LSC
Adsorbent dosage (g)		0.10	96.90 ± 0.06	97.40 ± 0.28
		0.25	98.40 ± 0.12	98.90 ± 0.46
		0.50	99.10 ± 0.18	99.70 ± 0.61
pH	0.25 g	3	61.80 ± 0.18	65.10 ± 0.56
		5	91.80 ± 0.26	92.50 ± 0.67
		6	96.40 ± 0.17	97.90 ± 0.64
		7	95.90 ± 0.12	96.60 ± 0.36
	0.5 g	3	62.80 ± 0.16	67.20 ± 0.71
		5	92.20 ± 0.32	94.10 ± 0.92
		6	99.00 ± 0.25	99.80 ± 0.86
		7	97.60 ± 0.26	98.10 ± 0.26
Contact time (min)		15	80.50 ± 0.17	82.10 ± 0.23
		30	90.50 ± 0.45	94.10 ± 0.75
		60	96.80 ± 0.16	96.50 ± 0.86
		100	97.30 ± 0.64	98.80 ± 0.09
Concentration (mg/L)		50	90.90 ± 0.61	91.90 ± 0.09
		100	88.85 ± 0.29	90.50 ± 0.27
		150	86.33 ± 0.45	87.67 ± 0.87
		250	76.20 ± 0.66	78.20 ± 0.68

average value

3.3 Effect of adsorbent dosage

One of the parameters that strongly affects the sorption capacity is the weight of the adsorbents. With the fixed metal concentration, it can be easily inferred that the percentage of removal of metal ions increases with increasing weight of the adsorbents as shown in Table 1. The results show that the weight of both species of cocoons of 0.50 g weight exhibited the ability to adsorb Pb(II) better than the weights of 0.25 and 0.10 g, respectively. However, LSC showed the maximum Pb(II) removal at 99.70% and TxC showed the maximum Pb(II) removal at 99.10%. As the number of cocoons increases, the surface adsorption increases, resulting in Pb^{2+} ions being able to adsorb more amino acids as well. The comparison of the adsorption efficiency of both species is illustrated in Fig. 3.

Fig. 3. Comparison of effect of adsorbent dosage on Pb(II) removal.

The results show that the Pb(II) adsorption efficiency of LSC was higher than that of TxC due to the fact that LSC has a much more adsorbent surface area than TxC when compared to the same adsorbent dosage. This may be due to the fact that LSC has higher fibroin content than TxC, allowing Pb^{2+} ions to adsorb more efficiently. This reason is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent [10]. Furthermore, an increase of the adsorbent amount resulted in the higher adsorption percentage owing to more adsorbed position. However, 0.25 g of fibroin is sufficient for adsorption, exhibiting almost 100% adsorption efficiency. Therefore, the cocoon weight of 0.25 g was selected to study the effect of contact time and solute concentration.

3.4 Effect of pH value

pH is an important controlling parameter for adsorption of metal ions because it affects the solubility of metal ions, concentration of the counter-ions on functional groups of the adsorbents and the degrees of ionization of the adsorbates during a reaction. The results of the effect of pH of lead(II) adsorption efficiency of the two cocoon species are shown in Table 1. The results of the comparison of Pb(II) removal at different pH conditions showed that in the first period, the adsorption efficiency of Pb(II) at pH 3 showed very low adsorption efficiency. The heavy metal cations are completely released in extreme acidic conditions. At lower pH values, the H^+ ions compete with the metal cation for the adsorption sites in the system [11]. In addition, when increasing the base condition at higher pH, the Pb(II) removal increases accordingly until both species of cocoons showed the highest Pb(II) removal at pH 6. It was found that LSC and TxC with the weight of 0.50 g showed the maximum Pb(II) removal at 99.80% and 99.00%, respectively. While, the weight of 0.25 g showed the maximum

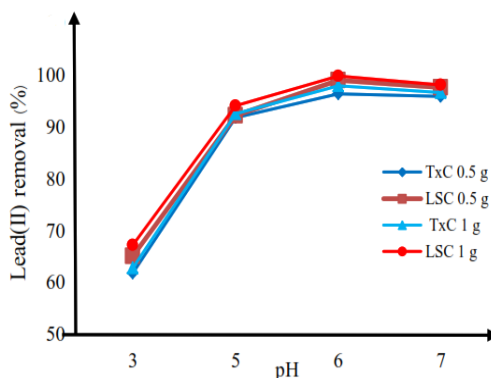Pb(II) removal at 97.90% and 96.40% for LSC and TxC, respectively, as shown in Fig. 4.

Fig. 4. Comparison of effect of pH on Pb(II) removal.

It was found that both species of cocoons showed the highest Pb(II) removal at pH 6, since the acidic condition of the solution influences the surface charge of the adsorbents and metal ions, which are dissolved in solution. If the solution has a pH lower than the isoelectric point, which has high acidity, as in the case of pH 3 and 5, the fibroin surface shows a positive charge, resulting in repulsion with the positive charge of Pb(II) ion. In addition, at high acidic conditions, there is a high amount of H^+. It is possible that there is a competition between H^+ and Pb^{2+} in combination with N-H of fibroin, resulting in the Pb^{2+} to be less adsorbed with the active site. While the solution condition with a pH higher than the isoelectric point causes the surface of the fibroin to show more negative ions, resulting in more adsorption with Pb^{2+} based on the electrostatic attraction. However, at pH higher than or equal to 7, the ions of Pb^{2+} react with OH^- and form sediment $Pb(OH)_2$. Therefore, pH 6 is the most suitable adsorption condition that does not conflict with H^+ or OH^- giving Pb^{2+} ions the opportunity to completely bind to the fibroin in the cocoons [2].

3.5 Effect of contact time

The adsorption of Pb^{2+} was studied as a function of time in order to find out the equilibrium time required for maximum adsorption of metallic ions. The results of the effect of contact time on Pb(II) removal of the two cocoons for different times of soaking the biosorbents are shown in Table 1 and Fig. 5. The results show that the Pb(II) removal tends to increase steadily with the duration of soaking the cocoon adsorption material in the solution until at 100 min, both cocoons exhibited the highest Pb(II) removal. LSC produced (II) removal at 98.80% while TxC showed Pb(II) removal at 97.30%. However, the adsorption efficiency of both cocoons is similar. Due to the longer period of time, Pb^{2+} ions have more time to bond with the amino groups of the fibroin located on the surface of cocoons, resulting in complete adsorption. It is observed that the concentration of lead(II) ions adsorbed on the cocoons increased with time. This is also due to the migration of a higher fraction of metal ions from the bulk solution through the adsorbent boundary layer onto the active sites of the biosorbents as time progresses as illustrated in Fig. 5.
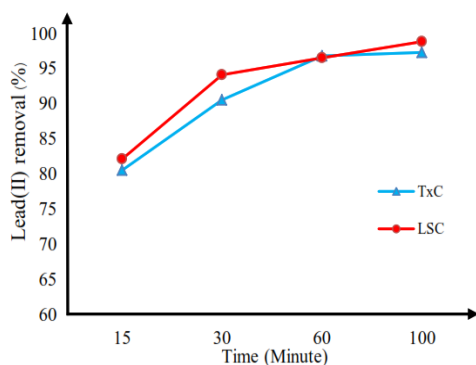

Fig. 5. Comparison of effect of contact time on Pb(II) removal.

The initial faster rate may be due to the availability of the uncovered surface area of the adsorbents since the adsorption depends on the surface area of the adsorbents. The Pb^{2+} adsorption took place at the more reactive sites. As these sites were progressively filled, the more difficult the sorption becomes, and the sorption process tends to be more unfavorable. This is the general characteristic of the adsorption of metal ions [2].

3.6 Effect of solute concentration

The effect of initial concentration on the Pb(II) removal was investigated and the removal of Pb(II) ions by both cocoons was found to decrease with an increase in initial Pb(II) concentration as illustrated in Fig. 6. The Pb(II) removal decreases from 91.90% to 76.20% when initial metal ion concentration is raised. At a lower concentration of 50 mg/L, maximal Pb(II) removal was due to the availability of many active sites on the surface of cocoon adsorbents. However, with an increase in concentration, surface active sites got saturated with metal ions and resulted in decreased removal of Pb(II). Similar results were given in the case of nano-adsorbent of Oryza sativa husk [9,12]. The observed behavior can be attributed to the increase in the amount of Pb(II) ions to the unchanging number of available fibroin active sites on cocoon adsorbents. Hence, more metal ions were left in solution. Thus, it can be inferred that the removal of the Pb(II) ion is highly concentration-dependent.
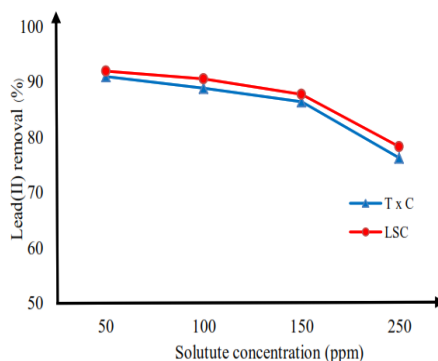

Fig. 6. Comparison of the effect of solution concentration on lead(II) removal.

3.7 Kinetic study

The transport rate mechanism of adsorbate in adsorbent is provided by kinetic data. Langergran's pseudo first order and Ho's pseudo second order [13] kinetic equations were used to describe kinetics of Pb(II) on to cocoon adsorbents. Representation of order is given by equations (3.1) and (3.2), respectively:

$$\log q_e - q_t = \log q_e - \left(\frac{k_1}{2.303}\right)t, \quad (3.1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}} + \frac{t}{q_e}, \quad (3.2)$$

where k_1 (min^{-1}) is pseudo first-order rate constant and k_2 (mg/ g min^{-1}) is pseudo second-order rate constant in adsorption kinetics, q_e (mg/g) and q_t (mg/g) are adsorption capacities per unit weight at equilibrium and at any time t. Equation (3) can be drawn from $\log(q_e - q_t)$ vs t plots which gives k_1 and q_e values. Equation (4) can be drawn by slope and intercept of the plot which gives values of k_2 and q_e. Experimental data for both the kinetic models represent high correlation coefficients. Comparing the values of correlation coefficient for both the models indicate that R^2 (0.9998 and 0.9998 of TxC and LSC, respectively) for pseudo second-order is higher than R^2 (0.8876 and 0.9567 of TxC and LSC, respectively) of pseudo first-order as depicted in Table 2. It is indicative of a better fit of Pb(II) adsorption data into pseudo second-order kinetics. Furthermore, Pb(II) removal results indicate that adsorption may be a rate limiting step that possesses valence forces among adsorbent and adsorbate with exchange or share of electrons [14].

Table 2. Parameters for lead(II) adsorption onto cocoon through kinetic models.

Adsorbent	Pseudo-first order			Pseudo-second order		
	q_e (mg/g)	k_1 (t/min)	R^2	q_e (mg/g)	k_2 (g/mg/min)	R^2
TxC	1.0805	0.0332	0.8876	20.1207	0.1890	0.9998
LSC	3.8806	0.0569	0.9567	20.2429	0.1958	0.9998

3.8 Adsorption experiments study

The experimental data for lead(II) ion uptake and heterogeneity or homogeneity of adsorbent was justified by adsorption isotherm models including Langmuir [15] and Freundlich [16]. Representation of models in linear form is given by equations (3.3) and (3.4) respectively:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}}, \quad (3.3)$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e, \quad (3.4)$$

where, q_{max} (mg/g) is maximum monolayer adsorption capacity, b (L/mg) is Langmuir constant. The linear plot was derived between C_e/q_e versus C_e to calculate adsorption parameters. K_f (mg/g (L/mg)$^{1/n}$) is Freundlich constant associated with adsorption capacity and n is heterogeneity factor. The K_f and n values were calculated from the linear plot drawn between $\log q_e$ versus $\log C_e$. The n value should lie between 1 and 10 for favorable adsorption. The values of adsorption parameters and correlation coefficient are given in Table 3.

Table 3. Langmuir and Freundlich constants for Pb(II) adsorption using cocoons.

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	b (L/mg)	R^2	K_f	$1/n$	R^2
TxC	51.8135	0.0474	0.9997	4.3102	0.5561	0.9673
LSC	52.3560	0.0541	0.9996	4.7468	0.5508	0.9635

Comparative correlation coefficient (R^2) values 0.9997 and 0.9996 of Langmuir model for TxC and LSC, and 0.9673 and 0.9635 of Freundlich model indicate fitness of the adsorption data as shown in Figure 7. The adsorption process of Pb(II) on both cocoons can be described by Langmuir isotherm. The adsorbed Pb(II) ions form a monolayer onto biosorption surface with a certain position on the surface [17]. The maximum adsorption capacities (q_{max}) of TxC and LSC are 51.8135 and 52.3560, respectively. In addition, the q_{max} of LSC was slightly higher than TxC for Pb(II) removal. The reason is probably the main functional group such as carbonyl or amino contents in the structure of LSC are higher than in TxC. Therefore, LSC has more metal-binding active sites and more negative surface, which enhances the retention of Pb(II) onto the surface.
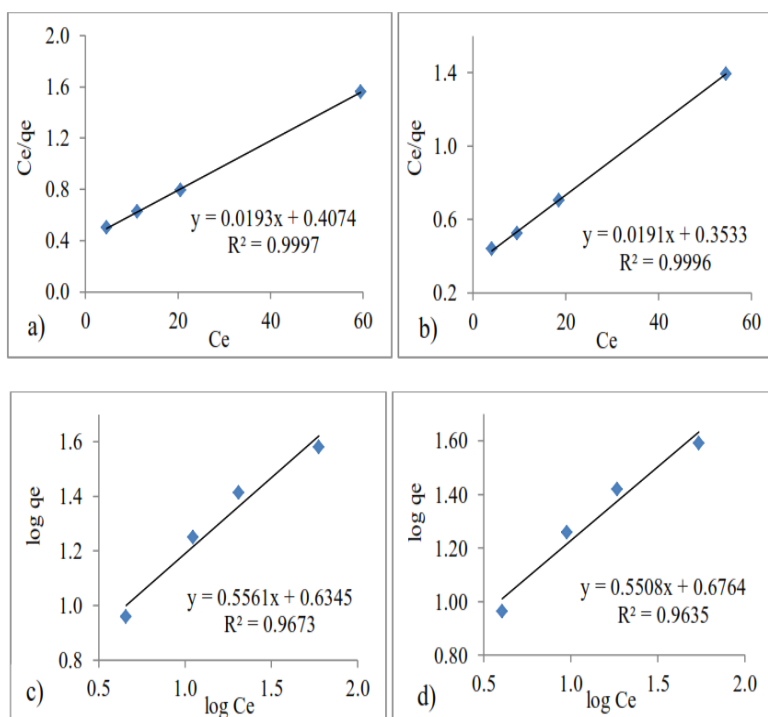
Fig. 7. (a, b) Langmuir isotherm (c, d) Freundlich isotherm for Pb(II) adsorption using cocoons.

3.9 Comparison of adsorption efficiency of biosorbents

Interestingly, it was found that the physical characteristics such as shades and surface characteristics of cocoon adsorbents after the experiment process to study the effect of all parameters can still maintain the adsorbent material very well as shown in Fig. 8. For this reason, they can be used to remove heavy metals in wastewater repeat-

edly. Therefore, it is a material that is suitable for application and is considered as the most efficient use of natural adsorbent materials.

(a) TxC   (b) LSC

Fig. 8. Physical characteristics of biosorbents after experiment.

Our results are consistent with the results of other groups. For example, Sombatsri et al. [18] studied the biosorption of Cu(II) ions onto fibroin powder obtained from cocoon. 50 mg/L Cu(II) ions solution of pH 6, temperature of 30 °C, adsorption time of 60 min and 0.50 g of fibroin powder, about 98% of Cu(II) ions were removed from the solution. Moreover, when comparing the effect of concentration of adsorption efficiency of Pb(II) in this work and Cu(II) ions of 50 mg/L, it was found that the maximum Pb(II) removal showed 99.70% and 99.10% for both cocoons, while Cu(II) showed the maximum Cu(II) removal at 98% (24.8 mg/g).

Godiya et al. [19] reported a sustainable and low-cost silk fibroin (SF)/polyethylene- imine (PEI) composite hydrogel for the remediation of heavy metal ions in aqueous solutions. The SF/PEI hydrogel demonstrated excellent adsorption capacities for the Cu(II), Pb(II), Cd(II), Zn(II), Ni(II), and Ag(I) ions, which were 163.9, 185.2, 169.5, 125.0, 140.8, and 200.0 mg/g, respectively. Based on the functional SF/PEI hydrogel, engineering for the cascaded treatment procedure will provide an effective and practical paradigm for the treatment and recycling of heavy metal ions in the wastewater.

Gao et al. [20] investigated modified water-insoluble silk fibroin (MWSF) membrane prepared by co-blending and interaction of fibroin and silane coupling agent. The sorption behavior of MWSF membrane for six metal ions, Cu(II), Co(II), Ni(II), Cr(III), Pb(II) and Cd(II), were measured. MWSF membrane had the significantly selective sorption for Pb(II) and Cd(II) metal ions and the removal percentage being 82% and 56%, respectively. Yalçın et al. [21] studied that silk fibroin (SF)/nylon-6 nanofiber matrices formed by electrospinning. Adsorption results showed that the removal efficiency of copper could reach 32% by continuous flow system whereas 77% by batch system. Ki et al. [22] examined SF and WK/SF blend nanofibrous membranes that were performed with Cu^{2+}. Furthermore, its adsorption capacity has been maintained after several recycling processes (desorption and re-adsorption) which are very advantageous as an affinity membrane. The electrospun WK/SF nanofibrous membrane is very suitable for removing and recovering heavy metal ions in water.

Zhou et al. [23] studied that silk fibroin (SF)/Cellulose Acetate (CA) blend nanofibrous membranes showed higher affinity for Cu^{2+} in an aqueous solution than pure SF and pure CA nanofiber membranes. Especially, the blend nanofibrous membranes with 20 % content of CA had an exceptional performance for the adsorption of Cu^{2+}, and the maximum milligrams per gram of Cu^{2+} adsorbed reached 22.8 mg/g. Aslani, Eral, & Akyil [2 4] investigated the basic features of thorium adsorption from aqueous systems by silk fibroin. Thorium(IV) adsorption proves to be very rapid and dependent on pH, temperature, retention time, concentration of ion, amount of fibroin, volume of solution and volume-to-mass ratio. Xiao et al. [8] examined ultrafine silk fibroin powder used as a low-cost adsorbent to remove dyes in the printing and dyeing wastewater. Results show that dye adsorption experiments demonstrated that silk powder could effectively remove model dyes. The batch experimental results sug-

gested that silk fibroin powder could be used as an efficient
sorbent to remove dyes in textile effluents.

As mentioned above, this information can be concluded that the adsorption efficiency of the different types of cocoon ad-

sorbents in various forms to adsorb heavy metals and the adsorption capacity of Pb(II) were compared with different studied natural cocoon adsorbents and encapsulated in Table 4.

Table 4. Adsorption of heavy metals in solutions using natural cocoon adsorbents.

Natural cocoon adsorbent	Heavy metal	Adsorption capacity	Reference
TxC Cocoon (TxC)	Pb(II)	51.8135 mg/g	This work
Lueang Surin Cocoon (LSC)	Pb(II)	52.3560 mg/g	This work
Silk cocoon	Cu(II)	24.8 mg/g (98%)	[18]
Silk fibroin (SF)/polyethyleneimine (PEI) composite hydrogel	Cu(II), Pb(II), Cd(II), Zn(II), Ni(II), and Ag(I)	163.9, 185.2, 169.5, 125.0, 140.8, and 200.0 mg/g	[19]
Silk fibroin (SF)/Cellulose Acetate (CA) blend nanofibrous membranes	Cu(II)	22.8 mg/g	[23]
Silk/Bentonite Clay Composite	Cd(II), Pb(II), Hg(II), and Cr(VI)	11.35, 11.1, 10.5, and 10.2 mg/g	[25]
Modified Water-insoluble silk fibroin (MWSF) membrane	Pb(II) and Cd(II)	82% and 56%	[20]
Silk fibroin (SF)/nylon-6 nanofiber matrices	Cu(II)	32%	[21]
Ultrafine silk fibroin powder	Methylene blue dye	20.58 mg/g	[8]
Bombyx mori silk cocoon	Na_2CO_3	24.4%	[26]

4. Conclusion

The aims of this study were to compare the adsorption capacity of two cocoon wastes, TxC Cocoon (TxC) and Lueang Surin Cocoon (LSC) for Pb(II) ions, and to investigate the effect of adsorbent dosage, pH, contact time and initial concentration in aqueous solutions. The optimum set of conditions for biosorption of Pb(II) ion were found to be adsorbent dosage 0.25 g, pH 6, contact time 100 min and initial concentration 50 mg/L, obeyed pseudo second order kinetic model. The adsorption data conformed to both the Langmuir and the Freundlich isotherms, but fitted best into the Langmuir model. Both cocoons adsorbed Pb(II) ions from aqueous solutions and the concentration of the metal ions adsorbed decreased with increases of concentrations, contact time, adsorbent dosage and pH. Therefore, it can be concluded that cocoons could serve as a cheap, readily available effective biosorbents for the removal of

Pb(II) from wastewater as a way of treatment before discharging into the environment.

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