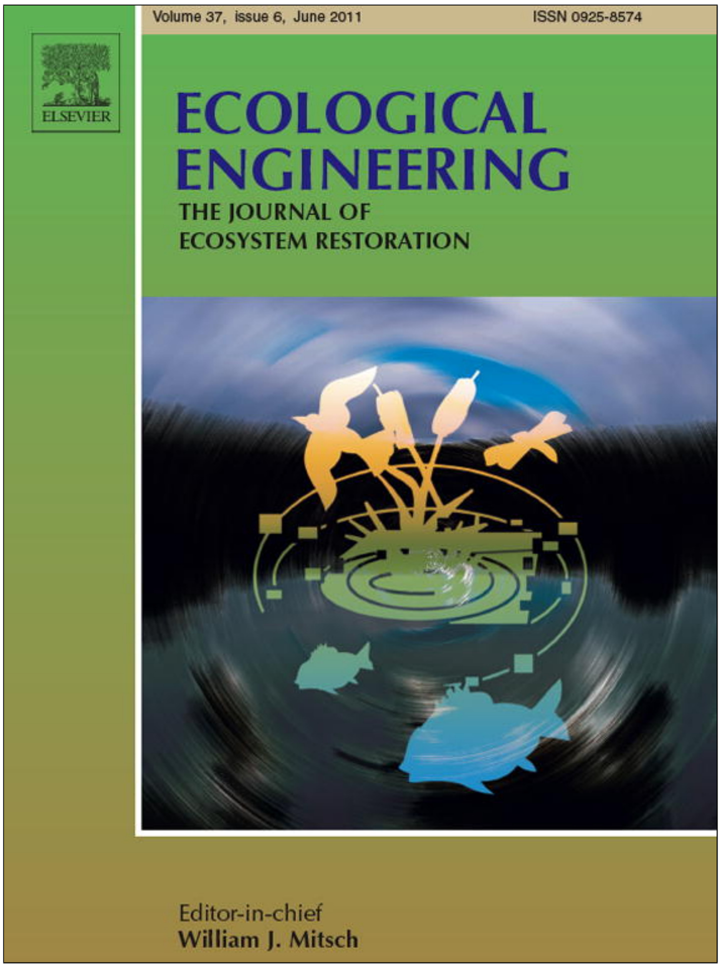
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Performance of durian shell waste as high capacity biosorbent for Cr(VI) removal from synthetic wastewater

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ABSTRACT

The capability of durian shell waste biomass as a novel and potential biosorbent for Cr(VI) removal from synthetic wastewater was studied. The adsorption study was performed in batch mode at different temperatures and pH. Langmuir and Freundlich isotherm models fit the equilibrium data very well ($R^2 > 0.99$). The maximum biosorption capacity of durian shell was 117 mg/g. On modeling its kinetic experimental data, the pseudo-first order prevails over the pseudo-second order model. Thermodynamically, the characteristic of Cr-biosorption process onto durian shell surface was spontaneous, irreversible and endothermic.

1. Introduction

Water contamination by heavy metal is a major concern for environmental preservation and human health. Chromium is a type of heavy metal originated from various industrial activities such as leather tanning, dye, mining, iron sheet cleaning, textile dying, cement industries and electroplating industries. Depending on the type of industry, chromium's concentration in wastewater may vary from about ten to hundreds of mg/L (Dakiky et al., 2002; Srivastava and Thakur, 2006; Bishnoi et al., 2007; Han et al., 2007; Malkoc and Nuhoglu, 2007; Ziagova et al., 2007). While Cr is obviously carcinogenic and possesses adverse potential to modify the DNA transcription process, it can also cause several diseases, like epigastria pain, nausea, vomiting, severe diarrhea, lung cancer, pneumonitis, allergic dermatitis, renal malfunction and hemorrhage (Pmila et al., 1991; Das and Guha, 2007; Han et al., 2007; Gokhale et al., 2008).

Ecological engineering is a very interesting multidisciplinary research field since the goal of this field is to repair the damage of ecosystem caused by various pollutants, including heavy metals pollution. The design of sustainable and balanced ecosystems between human society and environment is also one of the interest of this field (Asgher and Bhatti, 2010; Mitsch and Jørgensen, 2003). The restoration of an aquatic ecosystem contaminated by heavy metal using environmentally friendly adsorbent and a more economical method is one of the implementations of the ecological engineering.

A large variety of treatment methods to remove chromium are available, namely chemical precipitation and ion exchange (Malkoc and Nuhoglu, 2007), membrane separation (Chakravarti et al., 1995), electrochemical treatment (Kongsricharoern and Polprasert, 1996), reverse osmosis (Dakiky et al., 2002; Li et al., 2004), solvent extraction (Pagilla and Canter, 1999) and adsorption (Srivastava and Thakur, 2006; Razmovski and S'ciban, 2008). In the case of low chromium concentration, most of them are considered ineffective due to high capital and operational costs incurred besides its low removal efficiency. Adsorption, on the other hand, is already well-known for its selectivity and effectiveness on even a very low concentration of contaminants. Cost of adsorbent, however, serves as a barrier for its industrial application, as nearly all commercially available adsorbents are expensive. Numerous studies have been and are still being conducted to screen and pinpoint alternative adsorbents that can satisfy the industrial demand from both performance and economic perspectives, including different kinds of biomass.

In recent reports, numerous biomasses have been tested as alternative adsorbent to remove Cr(VI), including *Tamarindus indica*

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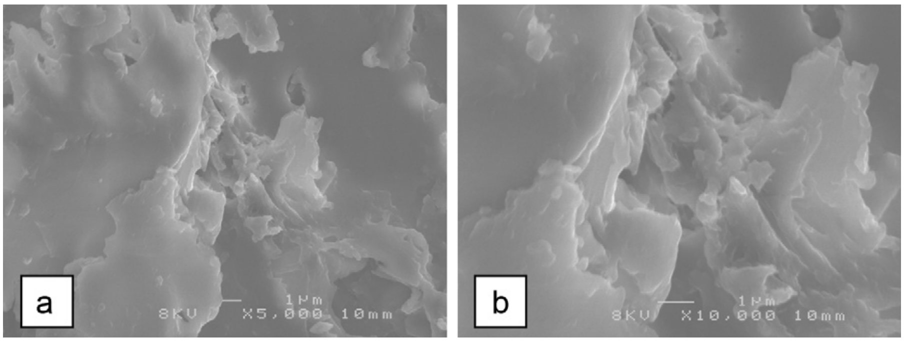

Fig. 1. SEM micrographs of pristine durian shell at two magnifications. (a) 5000× and (b) 10,000×

seeds (Agarwal et al., 2006), *Acinetobacter* sp. (Srivastava et al., 2007), waste tea fungus (Razmovski and S'ciban, 2008), cactus leaves, pine needles and wool (Dakiky et al., 2002), *Aspergillus sydoni* (Kumar et al., 2008), distillery sludge (Selvaraj et al., 2003), *Chlorella miniata* (Han et al., 2007), *Spirulina platensis* (Gokhale et al., 2008), *Eichhornia crassipes* (Mohanty et al., 2006), *Rhizopus arrhizus* (Preetha and Viruthagiri, 2007), *Saccharomyces cerevisiae* (Parvathi and Nagendran, 2007) and *Strepmoyces rimosus* (Chergui et al., 2007). Most of them have high adsorption capacity and therefore are worthy to be acknowledged. In order to be viable for industrial-scale application, however several criteria for adsorbent are required, namely (1) high adsorption capacity; (2) high availability in large quantity within one location; (3) low economical value (less advantage for other purpose); and (4) high reusability potential (attached metal can be easily removed). Indeed, nearly all of the mentioned alternative adsorbents already fulfilled 2 or 3 of these criteria. The second criterion imposes the most difficult condition for some microorganisms, as their isolation, screening and harvesting in large scale are complicated and very expensive, preventing their utilization in industry, unless they can be obtained as waste or by-product of an industrial fermentation process.

Although most biosorption studies have focused on finding a new alternative adsorbent, this spotlight is still considered important and attractive due to its interdisciplinary challenge, mystery of biomass–metal interaction and unsolved heavy metals threat towards the environment faced by most developing countries. As a developing country, Indonesia also faces a serious heavy metal pollution problem on its environment to the extent that many regulations have been issued by the Indonesian government. Direct discharge of waste and wastewater onto river and ground surface by most industry are still the main practice attributable to the economic constraints and lack of adaptable technology. To that end, leftover of durian shells which are commonly available in Indonesia abundantly (797,798 ton fruits are produced in 2009) without any further economic value are highlighted here to verify their potential employment as novel biosorbent so that they can be used further instead of ending as a mere waste.

This present study highlights various aspects of Cr-biosorption using durian shell waste as a novel and potential alternative biosorbent. The characterizations of pristine and Cr-loaded durian shell were given, followed by reliable metal biosorption equilibrium and kinetic experimental data presentation, which collaborated with its thermodynamic properties.

2. Materials and methods

2.1. Materials

All reagents used in this study ($K_2Cr_2O_7$, 1,5-diphenylcarbazide, $NaHCO_3$, NaOH, Na_2CO_3, HCl, $Na_2B_4O_7$, $H_2C_2O_4$, and NaCl) were purchased at PT. KurniaJaya Multisentosa as analytical grade and directly used without any further treatment.

2.2. Preparation of biosorbent

Durian shell (Monthong variety) was used as biosorbent in this study. It was obtained and collected as solid wastes from durian processing industry near Surabaya. After collection, they were washed repeatedly with tap water to remove physical impurities like surface dirt. Subsequently, they were cut-off into smaller size with knife and dried in vacuum oven (MEMMERT UM400) at 80 °C for 24 h. The dried durian shell then was grounded by micro hammer mill (JANKE and KUNKEL) and sieved into three different particle sizes of −30/+40, −40/+60, −60/+80 mesh. Finally, the durian shell powder was kept in desiccators for further experimental used.

2.3. Characterization of biosorbent

2.3.1. Boehm titration

The surface chemistry of biosorbent was determined using Boehm's titration method (Boehm, 2002). Boehm's titration procedure is conducted as follows: A known amount of durian shell (0.5 g) was introduced into several conical flasks which containing 50 cm^3 of 0.05 N: NaOH, Na_2CO_3, $NaHCO_3$, and HCl solution. Subsequently, the conical flasks then were sealed and shaken for 48 h at room temperature. The suspension then was decanted and filtered pass through Whattman 42 filter paper of which 10 mL of the remaining solution was titrated with 0.05 N HCl or NaOH, depends on the original solution used. The number of acidic groups was calculated under the assumptions that NaOH neutralizes carboxylic, phenolic, and lactonic groups; Na_2CO_3 neutralizes carboxylic and lactonic groups; and $NaHCO_3$ neutralizes only carboxylic groups. The number of basic sites presented on the biosorbents surface was determined from the amount of HCl that reacted with samples.

2.3.2. pH drift

The pH_{pzc} (point of zero charge) of biosorbent was determined using pH drift method (Faria et al., 2004). The pH drift procedure is described as follows: 50 cm^3 of 0.01 N NaCl solutions were prepared and placed in several conical flasks. The pH of these solutions was adjusted to value between 2 and 10 by adding 0.1 N NaOH or 0.1 N HCl solutions. Subsequently, 0.15 g of durian shell was added into each conical flask and shaken at room temperature for 48 h. After 48 h, the pH of solution was measured with digital pH-meter (Schott CG-825) and noted as pH_{final}. The pH_{pzc} of biosorbent is determined as the point where the curve pH_{final} versus $pH_{initial}$ crosses the line $pH_{final} = pH_{initial}$.

2.3.3. *FTIR spectroscopy*

The surface functional groups of biosorbent were analyzed using infrared spectroscopy method. The characterization of pristine and Cr-loaded durian shell was conducted in FTIR SHIMADZU 8400S using KBr pelleting technique and the biosorbent spectra were recorded in mid-IR wavenumber range (500–4000 cm^{-1}).

2.3.4. *Scanning electron microscopy (SEM) analysis*

SEM images of durian shells were recorded using JEOL JSM-6400F field emission SEM. A thin layer of platinum was sputter-coated on the samples for change dissipation during FESEM imaging. The sputter-coater (Eiko IB-5 Sputter Coater) was operated in an argon atmosphere using a current of 6 mA for 4 min. The coated samples were then transferred to the SEM specimen chamber and observed at an accelerating voltage of 10 kV, eight spot size, four aperture and 37 mm working distance.

2.3.5. *Energy dispersive X-ray (EDX) and X-ray elemental mapping*

EDX and X-ray elemental mapping was performed in JEOL JSM-6460 LA low vacuum analytical Scanning Electron Microscope equipped with an integrated JEOL Hyper mini-cup, 133 eV resolution, ultra thin window (UTW), SiLi crystal and Energy Dispersive X-ray Spectrometer. Integrated JEOL Analysis Station (v3.2) software was employed to collect and analyze the X-ray data. Samples were coated with custom-made carbon coater with carbon fiber. Acquisition conditions on the scanning electron microscope were 20 kV, 10 mm working distance and 30 s live time acquisition at approximately 10–15% dead time.

2.4. *Biosorption experiments*

The biosorption experiments in this study were conducted at initial Cr(VI) concentration of 200 mg/L. The Cr(VI) stock solution was prepared by diluting a fixed amount of potassium dichromate ($K_2Cr_2O_7$) with 1 L deionized water. Biosorption isotherm studies were carried out by adding various mass of durian shell (1–10 g) into a series of conical flasks, which containing 50 mL of metal solution. Subsequently, the conical flasks were placed in a thermostatic water-bath shaker (MEMMERT SV-1422) and shaken for 60 min with constant speed at 100 rpm. The biosorption isotherm experiments were also performed at four different temperatures (30 °C, 40 °C, 50 °C and 60 °C) and three different pH (2.5, 6.6, and 7.2). The residual Cr(VI) ions concentration in solution after sorption process was determined spectrophotometrically (SHIMADZU UV/Vis-1700 PharmaSpec) at $\lambda = 540$ nm using 1,5-diphenylcarbazide as the complexing agent in acidic solution. The total Cr-content in solution was determined by flame atomic absorption spectroscopy (SHIMADZU AA6200) at wavelength of 357.8 nm. The Cr(III) ions concentration in metal solution was calculated from the difference between the total Cr and Cr(VI) concentration.

To study the biosorption kinetics, 400 mL of metal solution with initial concentration of 250 mg/L was introduced into glass vessel (11 cm in inner diameter and 15 cm in height) and equipped with four glass baffles (1 cm in width). Subsequently, a known amount of durian shell (10 g) with certain particle size fraction (−30/+40, −40/+60 and −60/+80 mesh) were weighed analytically and added into the vessel. The glass vessel then was placed in thermostatic water-bath shaker for 60 min and heated up from room temperature to the desired operating temperature. The pH of solution was also adjusted to certain value (2.5, 6.6, and 7.2) by adding some amount of HCl 0.1 N or NaOH 0.1 N onto the vessel. This mixture then was agitated at 500 rpm. During the kinetic experiments, at predetermined intervals of time, the metal solution was withdrawn from the vessel (10 mL using volumetric pipette). Subsequently, the metal solution was diluted with deionized water, centrifuged (4000 rpm for 5 min) and analyzed immediately. All of biosorption experiments in this study were performed in triplicate and the average results are presented in this work.

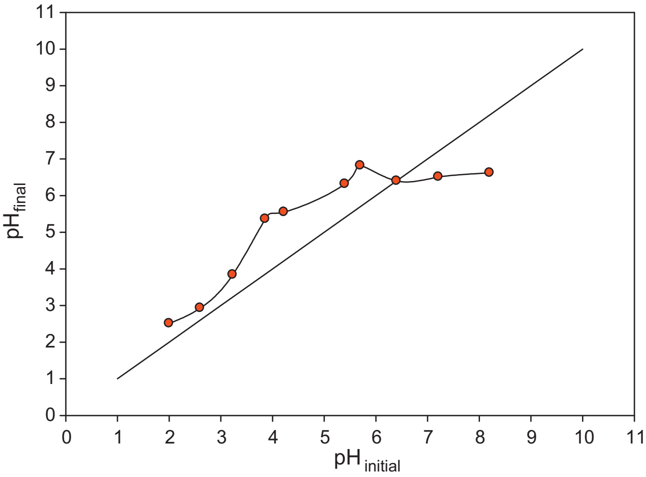

Fig. 2. pH_{pzc} determination of pristine durian shell.

The biosorption capacity of durian shell for Cr-metal removal at equilibrium state (q_e), in the unit concentration of mg g^{-1} or mmol g^{-1} can be determined by using following mathematic equation:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \qquad (1)$$

where m is the mass of durian shell used (g), V is the volume of metal solution (L), C_0 is the initial concentration of Cr-ions in solution (mg L^{-1} or mM) and C_e is the Cr-ions concentration in solution at equilibrium state (mg L^{-1} or mM).

3. Results and discussion

3.1. *Characteristics of pristine durian shell*

Physical characterization of durian shell was conducted by several analysis techniques. Scanning electron microscopy (SEM) was performed to determine the surface morphology of biosorbent. The SEM analysis of pristine durian shell at several magnifications was displayed in Fig. 1.

The surface oxides characterization by Boehm's titration method was performed to analyze the surface chemistry of biosorbent. The analysis result showed that the acidic surface oxides (carboxylic, phenolic, and lactonic) are more prevalent in durian shell (0.514 meq/g) compared with its basic surface oxides (0.117 meq/g). The acid nature of pristine durian shell was also confirmed from its pH_{pzc} value (Fig. 2).

The existence of surface functional groups on durian shell was also determined by FTIR technique, which the result was summarized in Table 1. The following wavenumbers appear in pristine durian shell: 653 cm^{-1} corresponded to the bending modes of C–H vibration in aromatic compounds; 1800–1990 cm^{-1} attributed to the C=O stretch of saturated aliphatic esters and carboxylic acids; 2170 cm^{-1} attributed to the C–C stretch of alkynes (–C≡C–) structure; 2673 cm^{-1} revealed to the C=O stretch of aldehyde groups (H–C=O) that may present in lignocellulosic compounds; 2943 cm^{-1} ascribed to the C–H stretching vibration of methylene ($-CH_2$) groups; 3363 cm^{-1} corresponded to the N–H stretch of primary or secondary amines and the last peak at 3905 cm^{-1} indi-

Table 1
Functional groups analysis of pristine and Cr-loaded durian shell by FTIR.

Functional groups	Wavenumber (cm^{-1})	
	Pristine	Cr-loaded
C–H bend (aromatic compounds)	653	675
C=O stretch (carboxyls)	–	1674
C=O stretch (saturated aliphatic esters)	1893	1857
C=O stretch (carboxylic acids)	1995	1988
C≡C stretch (alkynes)	2248	2250
C=O stretch (lignocellulosic compounds)	2673	2484
C–H stretch (methylenes)	2943	2950
N–H stretch (1° or 2° amines)	3364	3366
O–H stretch (alcohols or phenols)	3905	3891

cated the O–H stretch of free hydroxyls, either in alcohol or phenol groups.

3.2. Characteristics of Cr-loaded durian shell

To understand the biosorption of Cr-metal onto durian shell, the surface chemistry characterization of durian shell loaded with Cr(VI) ion was also performed using FTIR, Energy dispersive X-ray with scanning electron microscopy (SEM-EDX) and X-ray elemental mapping techniques.

The FTIR result for durian shell loaded with Cr(VI) ion was given in Table 1 while the spectra of pristine and Cr-loaded durian shell was shown in Fig. 3 for direct comparison purpose. The shifting of absorption peak, corresponded to C=O groups of aldehydes structure in lignocellulosic compounds from 2673 cm^{-1} to 2484 cm^{-1} was observed, a strong indication that this functional group was involved in the Cr(VI) ions binding. The lignocellulosic compounds in biomass have the ability to reduce Cr(VI) ions into Cr(III) ions in acidic condition (Fiol et al., 2008). The alteration of C–H stretch in methylene groups and O–H stretch bonded within alcohols or phenols, associated to their peak energy were also observed in Cr-loaded durian shell spectra, which also caused due to the binding of lignocellulosic materials with metal ions. Moreover, the presence of new absorption peak corresponded to C=O stretch of carboxyl groups was also noticed in the Cr-loaded durian shell spectra at wavenumber of 1674 cm^{-1}. The presence of this peak was contributed from primary alcohols and/or aldehydes oxidation by Cr(VI) anions in acidic condition, resulting in carboxyls formation, while Cr(VI) anions being reduced to Cr(III) cations. All of these phenomena indicate that reaction or binding between surface functional groups of durian shell with Cr-metal ions have already taken place and also imply that the metal biosorption process is not only relying on physical binding, but also on chemical binding.

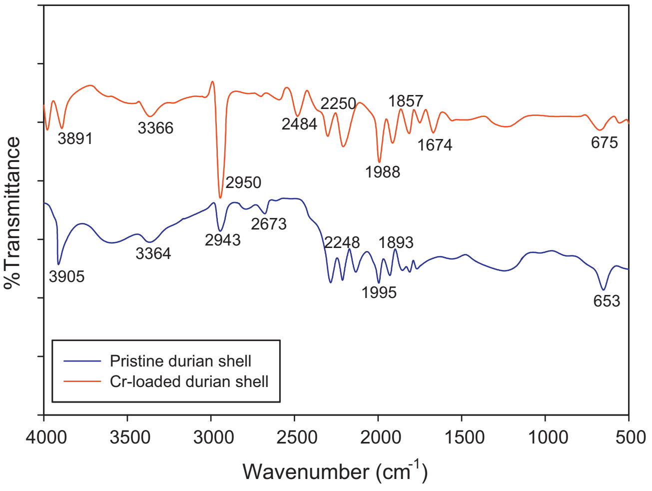

Fig. 3. FTIR spectra of pristine and Cr-loaded durian shell.

Energy dispersive X-ray (EDX) is a technique to analyze the element's presence based on its characteristic X-ray energy, commonly coupled with SEM. The SEM-EDX spectra of Cr-loaded durian shell were shown in Fig. 4. The Cr–K peaks confirmed the presence of Cr-ions on the biosorbent surface. The SEM and Cr-elemental X-ray elemental mapping at two spots are depicted in Fig. 5. The area that contains Cr(VI) ions was represented as bright region, most of which are not uniform, attributable to the non-uniformity of Cr(VI) ions distribution on the durian shell surface.

3.3. Biosorption isotherms

In this study, the two well-known isotherm models, Langmuir and Freundlich were chosen to represent and correlate the biosorption equilibrium experimental data. The fitted parameters of both isotherm models were calculated by non-linear regression method. The Langmuir isotherm model is expressed as follows:

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \tag{2}$$

While Freundlich isotherm model is expressed by following equation:

$$q_e = K_F . C_e^{1/n} \tag{3}$$

where q_{max} and K_L is Langmuir parameter represented the maximum biosorption capacity of biosorbent (mmol/g) and the equilibrium constant (L/mmol), respectively. On the other hand, K_F and n is Freundlich parameter represented the equilibrium constant associated to biosorption affinity $[(mmol/g)(L/mmol)^{1/n}]$ and the system heterogeneity, respectively. The fitted parameters of Cr-biosorption equilibrium experimental data by Langmuir and Freundlich isotherm model were summarized in Table 2.

In Table 2, it can be shown that both of Langmuir and Freundlich model could fit the experimental data very well, indicated from very good value of correlation coefficient ($R^2 > 0.99$). The highest Langmuir based maximum biosorption capacity (q_{max}) of durian shell is 2.25 mmol/g (117 mg/g) at pH 2.5 and 60 °C (Table 2). High percentage of Cr-metal ions removal at low pH was caused by the low content of Cr(VI) ions in solution due to the reduction of Cr(VI) into Cr(III) by lignocellulosic material in durian shell. For comparison purpose, the maximum biosorption capacity (q_{max}) of several alternative biosorbents which were used for uptaking Cr(VI) metal ions were also given in Table 3.

High adsorption capacity of Cr-metal ions onto durian shell at low pH value may also attribute to the presence of excess H^+ ions in solution which capable of partially neutralizing the negatively charged biosorbent surface, therefore reduces the hindrance for diffusion of Cr(VI) anions that majorly existed in dichromate ($Cr_2O_7^{-2}$) species onto biosorbent surface (Kumar et al., 2008). Increasing pH will enhance the electrostatic repulsion forces between Cr(VI) anions and negatively charged biosorbent surface, thus the removal of Cr-metal ions will be limited. Similar tendency has also been noticed by other authors in the biosorption of Cr(VI) by various biosorbents (Ahalya et al., 2005; Park et al., 2005; Mohanty et al., 2006; Anjana et al., 2007; Das and Guha, 2007; Garg et al., 2007; Malkoc and Nuhoglu, 2007; Isa et al., 2008; Li et al., 2008).

The q_{max} parameter magnitude in Langmuir isotherm seems to be increased by increasing the temperature, suggesting the enhancement of biosorption capacity at higher temperature. Furthermore, the K_L parameter, which related to binding affinity, also increase by increasing temperature which is a strong indication that the Cr-biosorption process has an endothermic nature

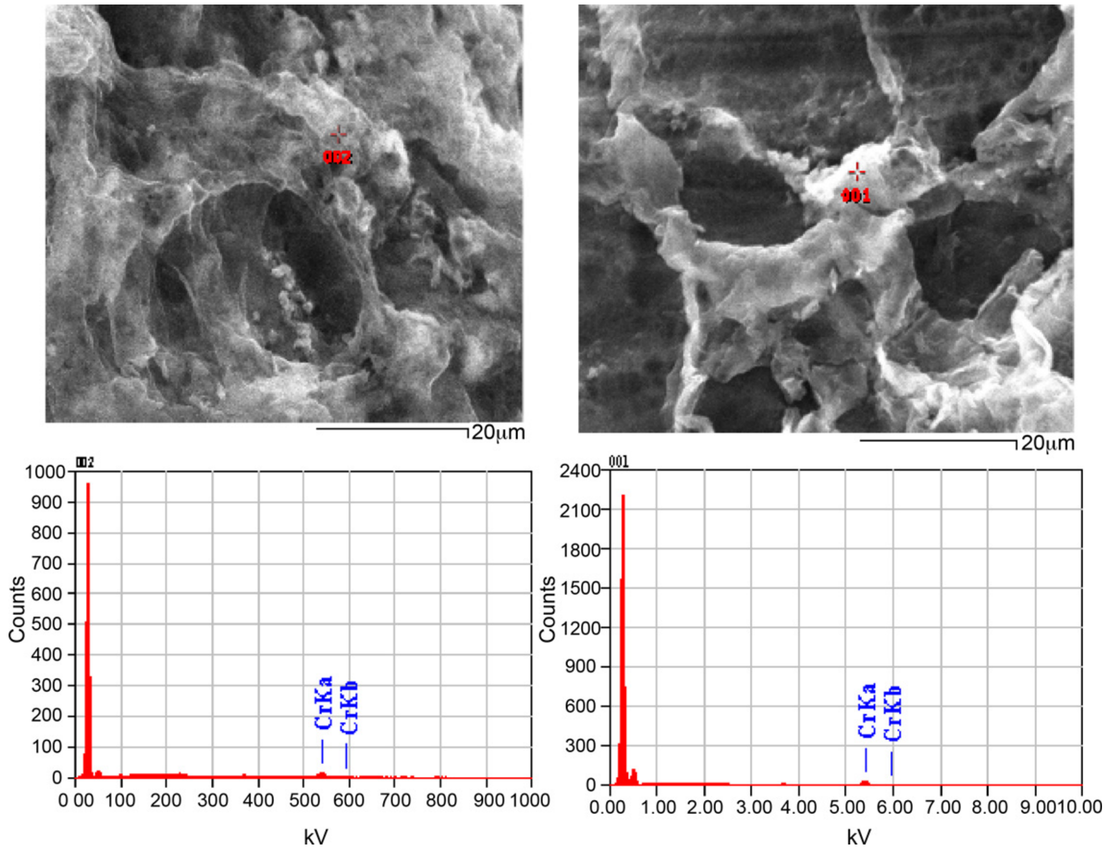

Fig. 4. EDX-SEM spectra of Cr-loaded durian shell.

and more favorable conducted at high temperature. The similar biosorption trends were also encountered in Freundlich isotherm, as the K_F parameter magnitude is also enlarged with temperature rise. Moreover, the enhancement of n parameter as the temperature increase suggests that the mobility of Cr-metal ions in solution was promoted due to greater contribution of kinetic energy hence increased the randomness degree and the heterogeneity of the system in bulk metal solution. All of these results clearly indicate that increasing the temperature will facilitate the penetration of Cr-metal ions onto durian shell surface; consequently the chemisorption process was predominant in this case.

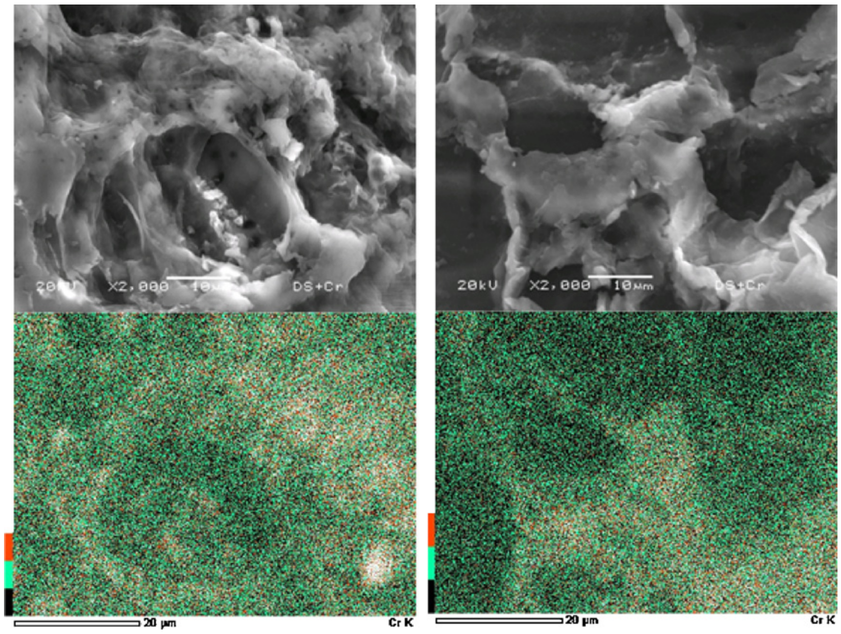

Fig. 5. SEM and X-ray elemental mapping analysis of Cr in Cr-loaded durian shell.

Table 2
The fitted parameter of isotherm models for Cr-biosorption using durian shell.

Isotherm model	Parameter	pH	Temperature			
			30 °C	40 °C	50 °C	60 °C
Freundlich	K_F (mmol/g) (L mmol^{-1})$^{1/n}$	2.5	0.1139	0.2890	0.6280	0.9891
	n		1.3608	1.6191	2.0385	2.3794
	R^2		0.9933	0.9965	0.9911	0.9887
Freundlich	K_F (mmol/g) (L mmol^{-1})$^{1/n}$	6.6	0.0266	0.0821	0.2059	0.3680
	n		1.3464	1.6397	2.0468	2.4375
	R^2		0.9913	0.9963	0.9901	0.9857
Freundlich	K_F (mmol/g) (L mmol^{-1})$^{1/n}$	7.2	0.0128	0.0504	0.1202	0.2486
	n		1.2908	1.6890	1.9991	2.4808
	R^2		0.9940	0.9950	0.9889	0.9812
Langmuir	q_{max}, mmol/g	2.5	1.3404	1.7352	1.9883	2.2487
	K_L (L mmol^{-1})		0.0799	0.1734	0.4617	0.9324
	R^2		0.9954	0.9956	0.9968	0.9919
Langmuir	q_{max}, mmol/g	6.6	0.5428	0.6973	0.8794	1.0348
	K_L (L mmol^{-1})		0.0385	0.0968	0.2497	0.5548
	R^2		0.9923	0.9970	0.9981	0.9960
Langmuir	q_{max}, mmol/g	7.2	0.3927	0.4667	0.6442	0.8215
	K_L (L mmol^{-1})		0.0247	0.0797	0.1619	0.3699
	R^2		0.9940	0.9934	0.9983	0.9977

3.4. *Biosorption kinetics*

Biosorption kinetics is provided vital information for determining and selecting optimum operational conditions for full-scale batch heavy metal removal process in industry. In this work, the pseudo-first order (Lagergren, 1898) and the pseudo-second order (Blanchard et al., 1984) kinetic models were employed to correlate kinetic experimental data. The pseudo-first order kinetic model has the mathematic form as follow:

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{4}$$

where q_t is the amounts of Cr-metal ions adsorbed per mass of durian shell used at time t (mmol/g), k_1 is the rate constant of pseudo-first-order reaction (min^{-1}) and t is time (min). The pseudo-second order kinetic model, on the other hand can be expressed in the following mathematic form:

$$q_t = q_e\left(\frac{q_e k_2 t}{1 + q_e k_2 t}\right) \tag{5}$$

where k_2 is the rate constant of pseudo-second order reaction (g mmol^{-1} min^{-1}).

The fitting of Eqs. (4) and (5) with kinetic experimental data were performed by non-linear least square method of which the resulting parameters of both kinetic models were tabulated in Table 4. As shown in Table 4, durian shell with smaller particle size gives higher removal of Cr-metal ion. It was also obvious that the rate constant (k) of both kinetic model was also enlarged for smaller particle fraction, to the extent that the equilibrium condition can be reached within shorter time. Accordingly, for a same amount of biosorbent, smaller particle size would contribute larger surface area so that more active binding sites of Cr-metal ion on the durian shell surface were exposed and available. In this study, the pseudo-first order represents kinetic experimental data better than pseudo-second order model as indicated in Table 4. This statement was confirmed from better value of correlation coefficient (R^2) of pseudo-first order rather than pseudo-second order model.

3.5. *Thermodynamics aspects*

With the aim to obtain complete features of the Cr-biosorption onto durian shell, the thermodynamic properties like standard Gibb's free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) of the biosorption process were also investigated. The standard Gibb's free energy change can be determined by following mathematical expression:

$$\Delta G^0 = -RT \ln K_L \tag{6}$$

where R is the universal gas constant (R = 8.314 J/mol K), T is the absolute temperature (K) and K_L is the Langmuir equilibrium constant (L/mol). To obtain the value of standard enthalpy change and standard entropy change, the K_L parameter can be expressed in terms of ΔH^0 (kJ mol^{-1}) and ΔS^0 (kJ mol^{-1} K^{-1}) as a function of temperature:

$$\ln K_L = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{7}$$

where the value of ΔS^0 and ΔH^0 is obtained from the intercept and slope on the plot of ln K_L versus 1/T, respectively.

The value of thermodynamic parameters of Cr-biosorption was reported in Table 5. Fig. 6 displayed the thermodynamic plot of ln K_L versus 1/T at different pH and temperatures. The Gibb's free energy change, in general indicates the spontaneity of the biosorption process (Ho and Ofomaja, 2006), in which the negative value suggests that the biosorption process is spontaneous. Increasing the temperature will lead to the more negative value of ΔG^0, which suggested that the metal biosorption process was favorable performed at higher temperature.

Table 3
The maximum biosorption capacity (q_{max}) of several biosorbents for Cr(VI) removal at certain operating condition.

Biosorbent	pH	T (K)	q_{max} (mg/g)	Reference
Rice straw	2	300.15	3.15	Gao et al. (2008)
By-product of *Lentinus edodes*	3.9–4.4	298.15	21.5	Chen et al. (2006)
LCS from wheat bran	2.1	298.15	37.4	Dupont and Guillon (2003)
Brown seaweed, *S. siliquosum*	3.6–4.2	303.15	15.9	Cabatingan et al. (2001)
Brown seaweed, *S. wightii*	3.5–3.8	298.15	38	Aravindhan et al. (2004)
Durian shell	2.5	333.15	117	Present study

Table 4
The fitted parameter of kinetic models for Cr-biosorption using durian shell.

pH	T (K)	Kinetic model	Parameter	Particle size fraction (mesh)		
				−30/+40	−40/+60	−60/+80
2.5	303.15	Pseudo-first order	q_e (mmol/g)	1.0482	1.1276	1.2137
			k_1 (min^{-1})	0.0799	0.0850	0.0874
			R^2	0.9876	0.9927	0.9931
		Pseudo-second order	q_e (mmol/g)	1.2567	1.3361	1.4306
			k_2 (g/mmol min)	0.0724	0.0752	0.0735
			R^2	0.9653	0.9764	0.9770
2.5	313.15	Pseudo-first order	q_e (mmol/g)	1.2268	1.2962	1.3481
			k_1 (min^{-1})	0.0814	0.0861	0.0948
			R^2	0.9870	0.9907	0.9870
		Pseudo-second order	q_e (mmol/g)	1.4648	1.5329	1.5715
			k_2 (g/mmol min)	0.0641	0.0667	0.0748
			R^2	0.9670	0.9740	0.9648
2.5	323.15	Pseudo-first order	q_e (mmol/g)	1.4832	1.5772	1.7039
			k_1 (min^{-1})	0.0738	0.0800	0.0839
			R^2	0.9852	0.9871	0.9853
		Pseudo-second order	q_e (mmol/g)	1.8069	1.8926	2.0260
			k_2 (g/mmol min)	0.0444	0.0479	0.0483
			R^2	0.9636	0.9653	0.9640
2.5	333.15	Pseudo-first order	q_e (mmol/g)	1.6691	1.8421	2.0342
			k_1 (min^{-1})	0.0693	0.0739	0.0788
			R^2	0.9827	0.9903	0.9923
		Pseudo-second order	q_e (mmol/g)	2.0583	2.2397	2.4421
			k_2 (g/mmol min)	0.0354	0.0361	0.0367
			R^2	0.9618	0.9712	0.9736
6.6	333.15	Pseudo-first order	q_e (mmol/g)	1.5268	1.5720	1.6377
			k_1 (min^{-1})	0.0603	0.0658	0.0705
			R^2	0.9902	0.9928	0.9948
		Pseudo-second order	q_e (mmol/g)	1.9302	1.9494	1.9904
			k_2 (g/mmol min)	0.0309	0.0352	0.0393
			R^2	0.9741	0.9792	0.9915
7.2	333.15	Pseudo-first order	q_e (mmol/g)	1.4674	1.5416	1.6213
			k_1 (min^{-1})	0.0667	0.0699	0.0756
			R^2	0.9875	0.9919	0.9945
		Pseudo-second order	q_e (mmol/g)	1.8203	1.8924	1.9581
			k_2 (g/mmol min)	0.0380	0.0395	0.0432
			R^2	0.9694	0.9753	0.9810

The positive value of the ΔH^0 denotes the endothermic nature of the metal biosorption process. Furthermore, the ΔH^0 value also indicates the adsorption type. Adsorption process with heat of adsorption between 2.1 and 20.9 kJ/mol is classified into physisorption while heat of adsorption between 20.9 and 400 kJ/mol is classified into chemisorption. Additionally, the activation energy parameter (${E_a}^0$) for chemisorption lies within the same range as the heat of chemical reaction, that is between 20.9 and 418.4 kJ/mol (Deng et al., 2006). As shown in Table 5, the positive value of ΔH^0 of biosorption process also strengthen earlier hypothesis that the mechanism of Cr(VI) biosorption onto durian shell surface was predominated by chemisorption. On the other hand, the positive value of ΔS^0 denotes the increased randomness at the solid–solution interface during metal binding process (Tan and Cheng, 2003; Ho and Ofomaja, 2006; Yavuz et al., 2006; Anber and Matouq, 2008; Aydin et al., 2008) beside its irreversibility characteristic, where as negative value of ΔS^0 represents the opposite phenomena (decreased randomness) (Ngah and Hanafiah, 2008).

Table 5
Thermodynamic parameters for Cr-biosorption using durian shell.

pH	T (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1} K^{-1})	R^2
2.5	303.15	−11.0413	70.1085	0.2674	0.9965
	313.15	−13.4228			
	323.15	−16.4825			
	333.15	−18.9393			
6.6	303.15	−9.2011	75.1823	0.2783	0.9996
	313.15	−11.9050			
	323.15	−14.8311			
	333.15	−17.5013			
7.2	303.15	−8.0824	74.2669	0.2723	0.9923
	313.15	−11.3990			
	323.15	−13.6670			
	333.15	−16.3785			

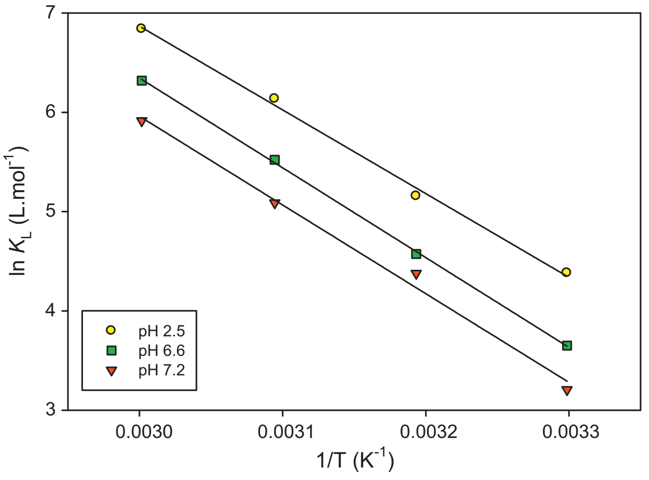

Fig. 6. Thermodynamic plot of ln K_L versus 1/T for Cr-biosorption using durian shell.

4. Conclusions

Durian shell waste was found to be one potential biosorbent candidate for Cr(VI) removal from wastewater. Both the Langmuir and Freundlich isotherm model could represent the biosorption equilibrium experimental data very well. The maximum biosorption capacity of durian shell was 117 mg/g at pH 2.5 and 60 °C. The pseudo-first order gave better correlation for fitting kinetic experimental data in comparison with pseudo-second order model. The investigation of biosorption isotherms and kinetics, in combination with thermodynamics aspects confirmed that the Cr-biosorption using durian shell waste was controlled by chemisorption which has endothermic ($\Delta H^0 > 0$), spontaneous ($\Delta G^0 < 0$) and irreversible ($\Delta S^0 > 0$) characteristic.

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