PERINTIS eJournal

PERINTIS eJournal, **2018**, Vol. 8, No. 2, pp. 86-101

BIOSORPTION OF CHROMIUM (VI) IONS USING SUSTAINABLE EGGSHELL IMPREGNATED PANDANUS AMARYLLIFOLIUS ROXB. ADSORBENT

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ABSTRACT

The conventional methods used for heavy metals removal from wastewater are cost inefficient and non-ecofriendly. Thus, biosorption using waste materials was proposed in this study. The study was carried out to remove chromium (VI), Cr (VI) ions using raw eggshell and hybrid eggshell-pandan biosorbent. The result obtained showed that the hybrid sorbent had higher efficiency in removal of Cr (VI) ions. The experimental results had indicated that in order to achieve the optimum Cr (VI) ions removal percentage of 17.78%, the optimum conditions required for the raw eggshell sorbent were 140 minutes of contact time, 0.5 g of sorbent, room temperature, pH 5 and initial concentration of 0.8 mg/L Cr (VI) ions solution. While for hybrid eggshell-pandan sorbent, an optimum removal percentage at 37.88% could be achieved when the contact time is 140 minutes, with 0.5 g dosage, 50°C, pH 4 and initial concentration of 0.8 mg/L Cr (VI) ions solution. The study showed that the adsorption of Cr (VI) ions onto the hybrid sorbent follows the pseudo-second-order kinetic model of Legergren, Freundlich isotherm model and the thermodynamic study showed negative values of Gibb's energy, positive value of enthalpy (16.68 kJ/mol) and entropy change (0.0473 kJ/mol). In short, the hybrid eggshell-pandan sorbent has greater potential as a biosorbent in removing Cr (VI) ions compared to that of raw eggshell sorbent.

Keywords: Eggshell, Pandan, Adsorption, Chromium (VI) ions, Biosorbent

1.0 INTRODUCTION

The presence of heavy metals as pollutants in water source is a major cause for global environmental concern. Most countries have set up guidelines and regulations for the discharge of wastewater containing heavy metal, so that the concentration of heavy metal can be controlled within a safe range. In order to achieve the standards and regulations, effluents are treated before discharging into water bodies. Cr (VI) ion is one of the most dangerous pollutants in aquatic environment due to its strong oxidizing capacity and dissolving power in water [1]. Chromium will not only cause cancer but it also leads to acute renal failure, haemolysis, immune system weakening, alternation of genetic material, liver and kidney damage, and also lung cancer [2]. According to Malaysia's Environmental Law, Environmental Quality Act, 1974, the Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, 1999, 2000, the concentration limit for chromium in effluent is 0.05 mg/L [3].

Some conventional wastewater treatment technologies are currently being used in removing heavy metal. However, most of those techniques were found economically and technically ineffective [4].With the advent of biosorbents, people started to use waste materials such as peanut shells and banana peels as biological adsorbents in wastewater treatment [5]. Global egg consumption has tripled in the past 40 years [6]. The high consumption of eggs correspond an increase in disposal of eggshells. Thus, the chicken eggshell is chosen to be used as an innovative adsorbent. To improve the effectiveness of eggshells as adsorbents, the eggshells will be impregnated with pandan extracts. Pandan leaves are used to enhance the odour of water treatment plant. Moreover, pandan plants can easily found throughout the year due to the tropical weather of Malaysia.

Biosorbents can be agricultural waste, industrial waste biomass, natural biomass or modified biopolymer. Biosorption process involves a solid phase, which is the adsorbent, and a liquid phase, that is the solvent which contains dissolved adsorbate (metal ions). During the adsorption process, the adsorbate will attach to the adsorbent by different mechanism depending on the affinity between two species. The degree of adsorbent's affinity towards the sorbate will directly alter the distribution of sorbate on adsorbent and in liquid when the process reaches equilibrium [7].

Due to the excellent combination of stiffness, strength, impact resistance and toughness, the eggshell and its membrane had been utilised in wastewater treatment [8]. Eggshell had been proven to have removal efficiency of more than 93% for iron, zinc, copper, chromium, manganese lead, and cadmium heavy metals [9]. In recent studies, the eggshell was modified by using α- FeOOH (F-ES) to detoxify Cr (VI) and phosphate from aqueous solution. For phosphate, the removal capacity was increased from 89.74 mg/g to 248.73 mg/g. Similarly for Cr (VI) ions, the efficiency was increased from 11.81 mg/g to 41.75 mg/g [1]. Extracted Pandanus amaryllifolius Roxb had been proven to have a moderate removal percentage on copper (III) ions removal [10]. However, in another research, pandan extracts had been used to enhance the Cr (VI) ions adsorption efficiency of chitosan adsorbent. Overall, chitosan showed very low removal of Cr (VI) ions with only around 30% removal while pandan extract showed a moderate efficiency of around 80% Cr (VI) ions removal. By using hybridised chitosan with pandan extracts, approximately 100% of Cr (VI) ions removal can be achieved [11].

The aim of this research is to synthesis a hybrid eggshell-pandan sorbent and compares the removal efficiency of this hybrid sorbent with that of raw eggshell sorbent. In the current study, the effect of reaction time, biosorbent dosage, temperature, pH of solution and initial concentration of metal ions solution on the removal efficiency of Cr (VI) ions were investigated. Also, the kinetic studies, adsorption isotherm model analysis and thermodynamic studies of the removal of Cr (VI) ions were studied.

2.0 METHODOLOGY

There were 4 phases in this study, starting with the preparation and synthesis of raw eggshell and hybrid eggshell-pandan sorbents. The second phase was where the characterisation of raw eggshell and hybrid sorbents were carried out. This is followed by the third phase which is to determine the effect of several parameters on the removal percentage of the ions. Lastly, the adsorption processes were investigated based on kinetic studies, adsorption isotherm model analysis and thermodynamic studies.

2.1 Materials

Fresh pandan leaves (P. amaryllifolius Roxb) were purchased from a local market at Taman Universiti, Skudai, Johor, Malaysia. The chemical being used in this experiment were raw eggshell, liquefied ethanol (C_2H_6O, 95% v/v), potassium dichromate powder, 0.1M solution of sodium hydroxide (NaOH), 0.1M solution of hydrochloric acid (HCl), distilled water, and deionized water. The chemicals purchased from Sigma Aldrich were of analytical grade and were used as received without further treatment.

2.2 Preparation of Sorbents

The chicken eggshells were isolated from kitchen waste and washed with deionized water. The eggshells were air-dried and incubated in hot air oven at 40°C for one day. Then, they were grinded into a powder form and sieved to obtain 106 μm particle size, before being kept in an airtight container.

Pandan leaves of approximately 200g was cleaned, cut into smaller pieces (approximately 3 cm) and immediately dried in an oven at 105°C for 24 hours. Then, the pandan leaves sample was grinded into 150 micron. Ethanol was used as the solvent for solvent extraction process , which was carried out for 24 hours. The permeate liquid obtained was placed on the hot plate at 80℃ to remove the remaining ethanol. 0.1 g of eggshell powder was dissolved in 50 mL of extracted pandan oil at room temperature. After 24 hours, the mixture was filtered and washed with deionized water to establish a neutral pH. Then, it was dried in oven at 110°C until a constant weight is obtained. The dried final product was the eggshell-pandan sorbent.

2.3 Characterization

Functional groups found within the sorbents were determined using Fourier Transform Infrared (FTIR) at room temperature with a spectral region of 400 cm^{-1} to 4000 cm^{-1} and a resolution at 2cm^{-1}. Scanning Electron Microscopy (SEM) was used to analyse the surface morphologies. Specific surface area of the sorbents was determined via Brunauer, Emmett and Teller (BET). The single point nitrogen adsorption-desorption isotherm at 403K (130°C) was introduced.

2.4 Adsorption Studies

2.4.1 Effect of Reaction Time

To investigate the effect of reaction time on the removal capacity of modified sorbent, parameters other than reaction time will be fixed. The initial concentration of solution was 0.8 mg/L, with 0.1 g of biosorbent dosage, at pH 4 and room temperature. The mixture was stirred continuously and the sample was collected for every 20 minutes until equilibrium was achieved. The concentration of Cr (VI) ions was determined by using a COD meter and Multiparameter Photometer. The efficiency of adsorption (%) was calculated using by Equation 1.

$$E\% = \frac{c_i - c_e}{c_i} \times 100 \tag{1}$$

where c_i is the initial equilibrium concentration of Cr (VI) (mg/L) in wastewater and c_e is the final equilibrium concentration of Cr (VI) (mg/L) in wastewater.

2.4.2 Effect of Biosorbent Dosage

Biosorbent (0.1 g) was added into 50 mL of 0.8 mg/L of chromium (VI) ions solution at pH 4 and room temperature. The sorption process was left stirring until the equilibrium time and the mixture was collected to be examined. The experiment was repeated using 0.3 g, 0.5 g, and 1 g. The dosage with the greatest removal percentage was used for the following sets of experiment.

2.4.3 Effect of Solution Temperature

Optimum biosorbent dosage was added into 50 mL of 0.8 mg/L of chromium (VI) ions solution. The condition was set at pH 4 and room temperature. The experiment was being repeated using different temperature of solution as 40°C, 50°C, 60°C and 70°C. The temperature that showed the highest efficiency in removing heavy metal was used in following experiments.

2.4.4 Effect of Solution pH

Optimum biosorbent dosage was added into 50 mL of 0.8 mg/L of chromium (VI) ions solution at pH 4 and optimum temperature. The experiment was repeated using pH values of 5, 6, 7 and 8. The pH value with the highest removal percentage was used in following experiments.

2.4.5 Effect of Initial Metal Ions Concentration

An experiment was done with optimum amount of biosorbent dosage at optimum pH and temperature. Optimum dosage of sorbent was added into 50 mL of 0.8 mg/L Cr (VI) ions solution. The experiment was repeated using 1 mg/L, 2 mg/L, 4 mg/L, and 8 mg/L solution.

2.5 Kinetic Models Analysis

Pseudo first-order model of Lagergren is established based on the assumption where the rate of change of adsorbed analyses with time is proportional to the difference in equilibrium biosorption capacity and the adsorbed amount [12]. Its equation can be expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where q_e and q_t are the amounts of adsorbate (mg/g) at equilibrium and at time t (min), respectively. While k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). For pseudo-second-order kinetic model of Lagergren, it can be applied with the assumption that the rate-limiting step involves chemisorption [13]. It can be represented as:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (3)$$

where q_e and q_t are the amounts of adsorbate (mg/g) at equilibrium and at time t (min), respectively. While k_2 is the rate constant of pseudo-second-order adsorption (min^{-1}). Other model is where usually the adsorbates species is transported from the bulk solution into solid phase through intraparticle diffusion process. It is expressed as follow:

$$q_t = K_{diff} t^{1/2} + C \quad (4)$$

where C (mg/g) is the intercept and K_{diff} is the intraparticle diffusion rate constant (mg/gmin$^{1/2}$). The q_t is a linearity correlation of $t^{1/2}$ and rate constant K_{diff} from the slope of regression line. In this model, three linear regions are found connected the bulk diffusion, intraparticle diffusion and adsorption at active site [14].

2.6 Adsorption Isotherm Model

Langmuir isotherm can be expressed as:

$$C_e/q_e = C_e/q_m + 1/(q_m b) \quad (5)$$

where q_e is the amount of ion adsorbed (mg/g), Ce is the equilibrium concentration of the adsorbate (mg/L),while q_m (mg/g) is the maximum adsorption capacity and b are Langmuir constants [15]. Freundlich isotherm described the adsorption occurs on heterogeneous surfaces and can be represented as:

$$log\ q_e = \frac{1}{n} log\ C_e + log\ K_f \quad (6)$$

where q_e is the amount adsorbed at equilibrium (mg/g), K_f is the Freundlich constant, 1/n is the heterogeneity factor which is related to the capacity and intensity of the adsorption, and C_e is the equilibrium concentration (mg/L) [15]. Temkin isotherm is established based on the assumption that the heat of adsorption is inversely proportional to the coverage of adsorbent due to the interaction between adsorbent and adsorbate and expressed as:

$$q_e = \frac{RT}{b} ln(A) + \frac{RT}{b} lnC_e = B\ ln(A) + BlnC_e \quad (7)$$

where B=RT/b is a heat sorption constant (J/mol) obtained from the graph q_e versus lnC_e. A is Temkin isotherm equilibrium binding constant (L/g), b is Temkin isotherm constant, R is the universal gas constant (8.314 J/mol K) and C_e is the equilibrium concentration (mg/L) [15].

2.7 Thermodynamic Studies

The thermodynamic parameters can be calculated by using equations below:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

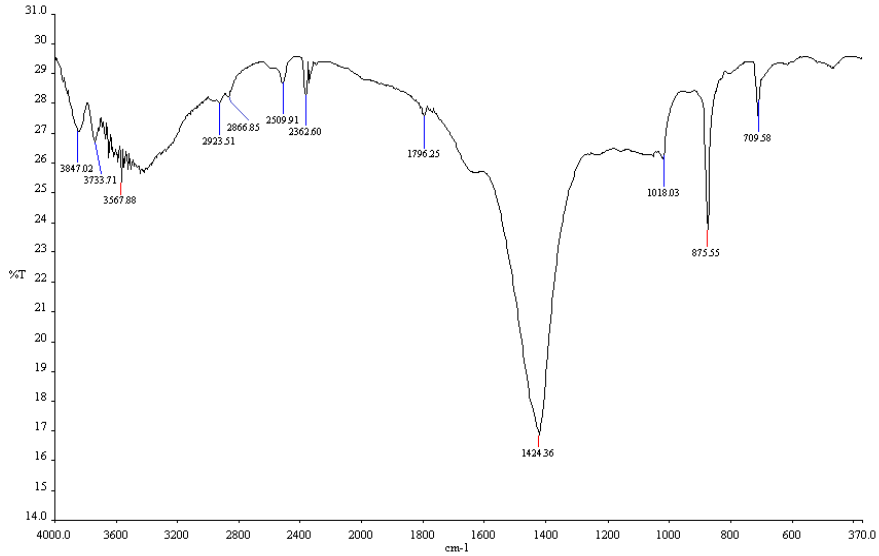
$$\Delta G° = - RT\ ln\ (K_d) \quad (9)$$

where q_e is the adsorption capacity at equilibrium. ΔG° is the standard Gibbs free energy change for the adsorption process (J mol^{-1}); R the universal gas constant (8.314 J/mol K), while T is the absolute solution temperature (K) [16].

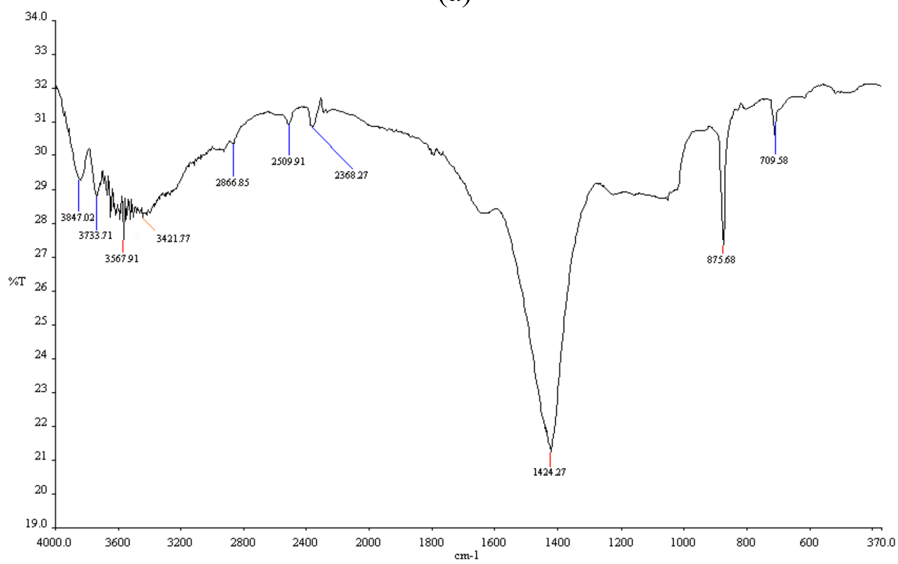
3.0 RESULTS AND DISCUSSION

3.1 FTIR Spectroscopy Analysis

The results of the Fourier Transform Infrared (FTIR) study for raw eggshell powder and hybrid eggshell-pandan sorbent is shown in Figure 1 (a) and (b).



(a)



(b)

Figure 1 IR spectrum of (a)raw eggshell and (b)hybrid eggshell-pandan sorbent

For raw eggshell powder, the adsorption peaks of CO_3^{2-} is observed at 1796.25, 1018.03, 875.55 and 709.58 cm^{-1} which indicated the stretching and bending of C=O. The band exhibited at 1424.36 and 2362.6 cm^{-1} correspond to the C=O stretching vibration thus proving calcite as the fundamental constituent of the eggshell [17]. In the high wavelength region, the most intensive peak is at around 3500 cm^{-1} followed by 3567.88 cm^{-1} which correspond to the bending and stretching mode of O-H and N-H groups respectively. The peaks at 1018.03, 1796.25 and 2923.51 cm^{-1} were missing in the hybrid sorbent because the 2-AP compound attached on the

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sorbent surface has masked some of the functional groups. The additional peak which appeared in the hybrid eggshell-pandan sorbent at 3421.77 cm^{-1} represents a secondary amine group in 2-AP compound.

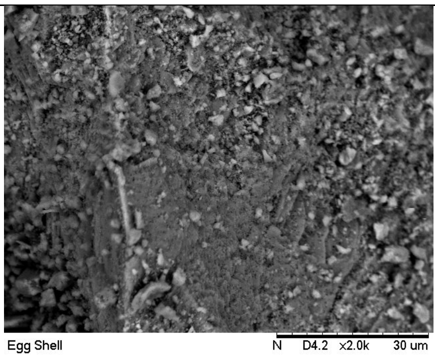
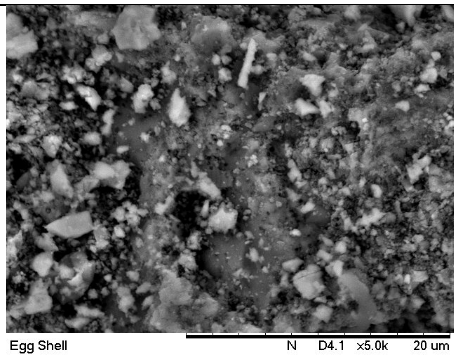
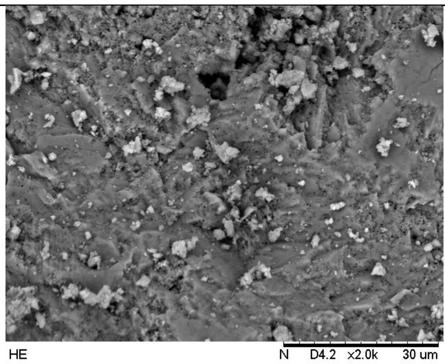
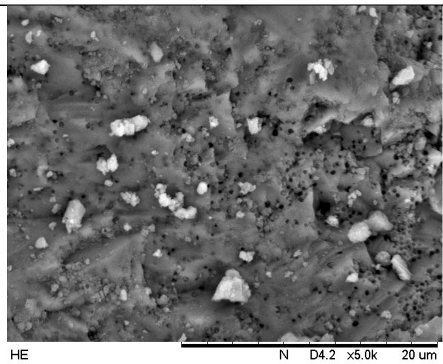
3.2 BET Analysis

The surface area of the raw eggshell and hybrid eggshell-pandan sorbent are 1.61 m^2/g and 0.46 m^2/g. This surface area of raw eggshell is almost similar to that of 1.05 m^2/g of eggshell [18]. The decrement in the specific surface area of the hybrid sorbent compared to that of the raw eggshell powder might be attributed to the covering of sorbent pores by 2-AP compounds.

3.3 SEM Analysis

SEM analysis shows the surface morphologies of the biosorbents. Table 1 illustrates the SEM photography of the raw eggshell sorbent and the hybrid sorbent both in powder form. The raw eggshell powdered particles have irregular crystalline structure and a wide particle size range was observed. Both adsorbents are proven to have small interspace structure which provide large surface area for adsorption. For the micrographs of the hybrid eggshell-pandan sorbent, there are many small compound attached on the eggshell surface. This had proven the successful impregnation process of 2-AP compound onto the eggshell surface.

Table 1 SEM Micrographs for different biosorbents at various magnitude

Sample	X 2000	X 5000
Raw Eggshell Sorbent		
Hybrid Eggshell-Pandan Sorbent		

3.4 Effect of Reaction Time on Cr (VI) Removal

Figure 2 shows the effect of reaction time on the biosorption of Cr (VI) ion. The interval of the reaction time is 20 minutes. By comparing both curves with different types of biosorbent, hybrid eggshell-pandan sorbent shows greater removal percentage of Cr (VI) ion (21.51%) than raw eggshell sorbent (13.12%).

Both biosorbents show a relatively great removal rate of metal ion at the beginning of removal process due to the highly available binding sites on the surface of sorbent. Then, the rate of adsorption gradually decrease with increasing reaction time as the gradient of the curve decrease. As the adsorption process goes on, the biosorbent surfaces are highly saturated, resulting in the diffusion of metal ions into the inner part of biosorbent and thus lowering down the rate of adsorption [16]. From the result, an equilibrium time of 140 minutes is sufficient to obtain the maximum chromium (VI) ions removal percentage.

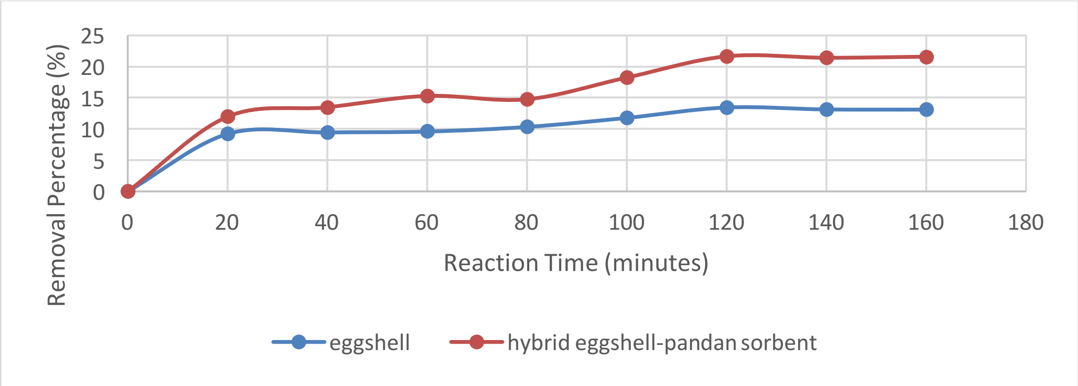


Figure 2 Effect of Reaction Time

3.5 Effect of Biosorbent Dosage on Cr (VI) Removal

The effect of sorbents dosage, ranging from 0.1 to 1 g was studied for a contact time of 140 minutes. Figure 3 indicates the similar trend for both biosorbent, where the Cr (VI) ions removal percentage increases as the dosage increase from 0.1 g to 0.5 g and reaches the maximum removal percentage at 0.5 g of biosorbent. The maximum removal percentage of Cr (VI) ions by 0.5 g of eggshell and hybrid sorbent are 17.9 % and 26 % respectively.

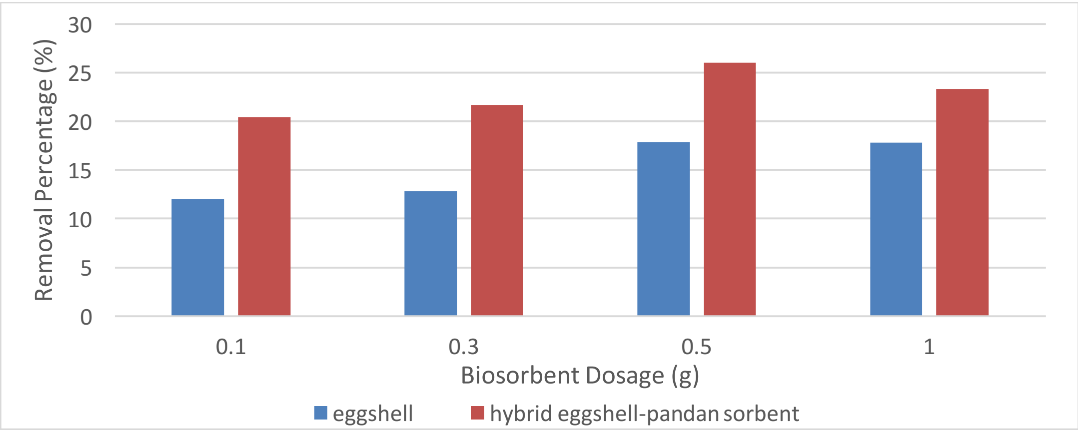


Figure 3 Effect of Biosorbent Dosage

The higher the biosorbent dosage, the greater the adsorbent surface areas, and thus augmenting the number of available adsorption sites [19]. The further increase of biosorbent dosage greater than 0.5 g lower the removal efficiency of chromium (VI) ions. This result fits with the theory because it reaches the equilibrium between ions and the biosorbent. The further increase over the optimum dosage will lead to screen effect between the sorbent particles [19]. 0.5 g of biosorbent of raw eggshell and hybrid eggshell-pandan are used as the optimum dosage.

3.6 Effect of Solution Temperature on Cr (VI) Removal

From Figure 4, raw eggshell has the highest removal efficiency at 25°C while hybrid eggshell-pandan sorbent exhibits greatest removal capability at 50°C. As expected, the hybrid eggshell-pandan sorbent shows higher Cr (VI) ions removal percentage than raw eggshell.

For the hybrid eggshell-pandan sorbent, the removal percentage shows an increasing trend when the temperature increases until 50 °C. The removal efficiency reaches the optimum at 50 °C with a Cr (VI) ions removal percentage of 37.3 %. As the surface activity and kinetic energy of the adsorbent increase, more metal ions are able to diffuse into the biosorbent and thus increasing the adsorption ability of the sorbent [16]. Further increase in temperature after 50°C leads to a slightly lower removal efficiency as denaturation of protein occurs [20].

For raw eggshell sorbent, the removal percentage decrease from 17.9 % to 6.4 % when the temperature increase from 25°C to 40°C. This significant decrease is due to the denaturation of the biosorbent at 40°C. The slight increment in percentage afterward is due to the fact that the driving force of the increasing kinetic energy is greater than the effect of biosorbent denaturation. Thus, 50°C and 25°C is the optimum temperature for raw eggshell and hybrid sorbent respectively.

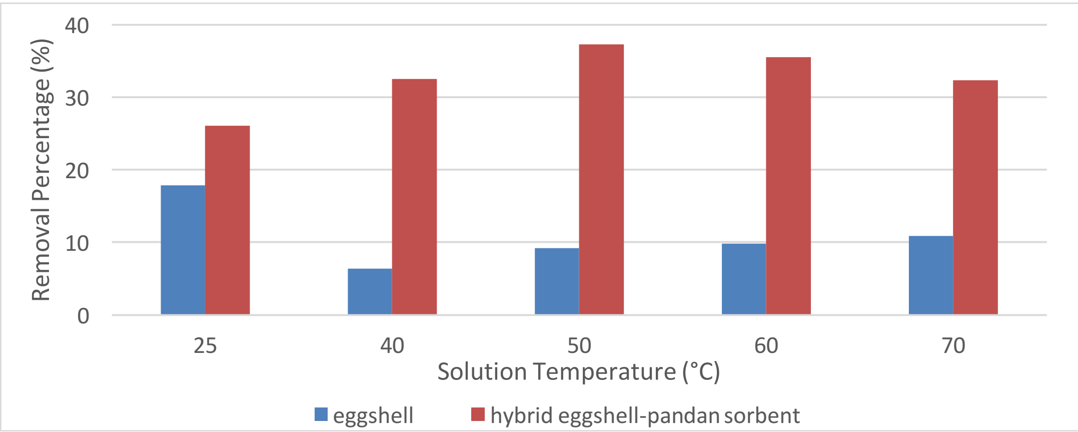


Figure 4 Effect of Solution Temperature

3.7 Effect of Solution pH on Cr (VI) Removal

The Cr (VI) ions adsorption capacity is doubled up from 16.8 % to 37%, after the eggshell was modified by hybridisation with pandan extract. As showed in Figure 5, the maximum adsorption percentage for hybrid eggshell-pandan sorbent is observed at pH 4. The removal capacity starts to decrease sharply when pH value is increased from the optimum value to pH 8. However, for raw eggshell sorbent, the highest Cr (VI) ions adsorption occurred when the adsorption process was conducted at pH 5. In acidic solutions, as the H^+ ions had protonated the amino groups, positively charged active sites will be present. This positive charge active site form an electrostatic attraction with Cr (VI) anions, $HCrO_4^-$. When the pH value of the solution increase, the concentration of OH^- increase and compete with metal anions, thus, lowering the removal percentage [21].

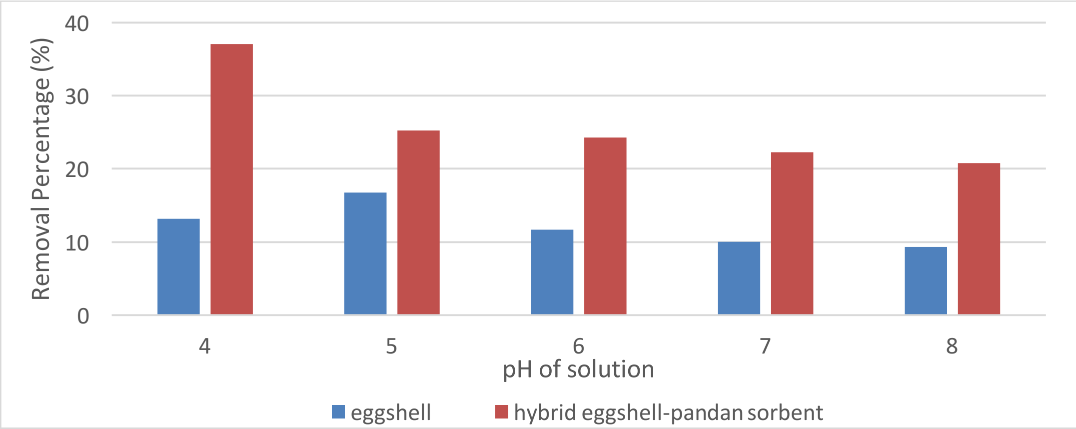


Figure 5 Effect of Solution pH

3.8 Effect of Initial Concentration on Cr(VI) Removal

Figure 6 clearly illustrates that the removal percentage of Cr (VI) ions had decreased from 17.78% to 8.23% for raw eggshell sorbent and from 37.88% to 16.1% for hybrid eggshell-pandan sorbent. Despite the decreasing removal percentage of Cr (VI) ions in the solution, the adsorption capacity of the biosorbent increases. The higher the initial metal ions concentration, the greater the driving force to overcome the mass transfer resistance [22]. Thus, the removal capacity of the adsorbent increases.

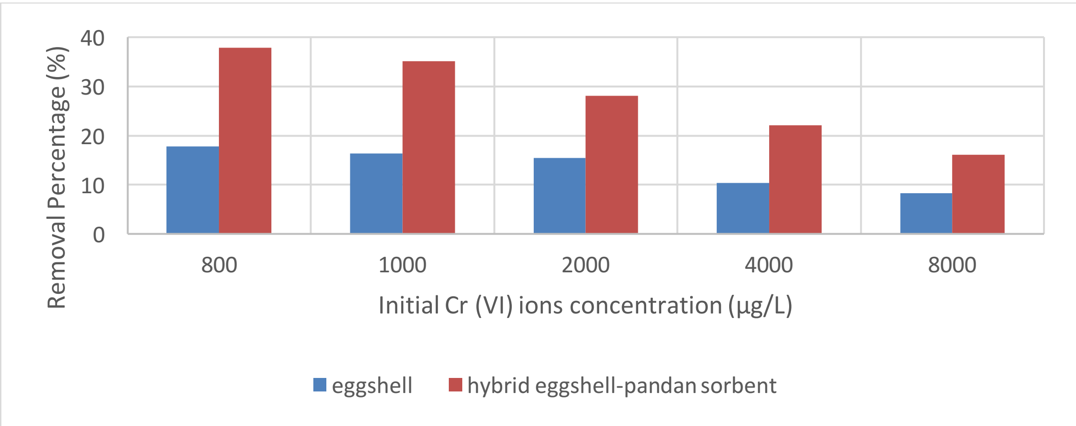


Figure 6 Effect of Initial Concentration of Solution

3.9 Adsorption Kinetic Studies

The adsorption data of chromium (VI) ions using hybrid eggshell-pandan sorbent is analysed using pseudo first-order, pseudo second-order kinetics models and intraparticles diffusion model. The data collected is used to plot graphs, corresponding to Equation 2, 3 and 4 as showed in Figure 7, 8 and 9 respectively.

The results prove that the pseudo-first-order model does not fit well for the whole range of the reaction time. This is because the surface of the hybrid eggshell-pandan sorbent is not homogenous. Figure 8 represents a relatively good fit over the whole range of contact time. Also, comparing with that of first order, the q_e calculated from the graph of pseudo-second-order is closer to the experimental value of q_e. This suggest that the biosorption may be the rate-limiting step that involve valence forces through sharing or exchange of electrons between sorbent and sorbate, which in turn involves chemisorption [23].

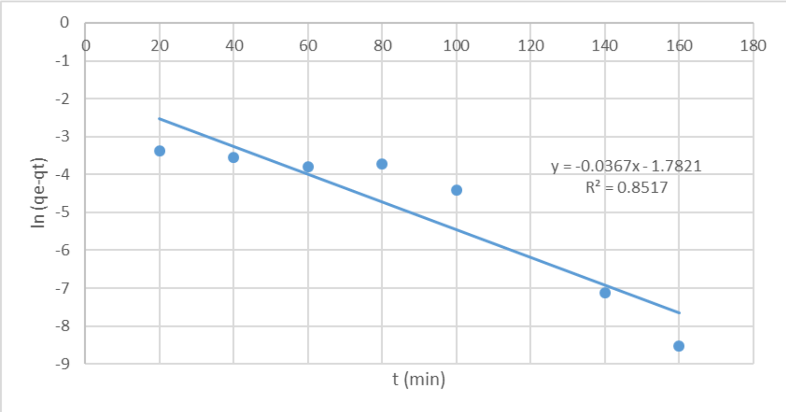


Figure 7 Pseudo-first-order Kinetic Model

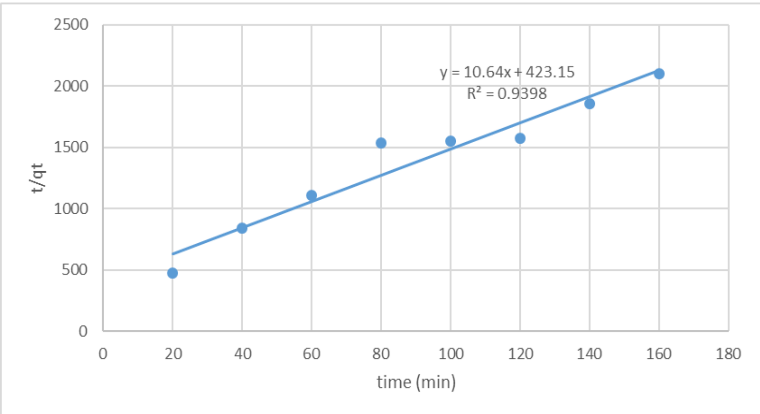


Figure 8 Pseudo-second-order Kinetic Model

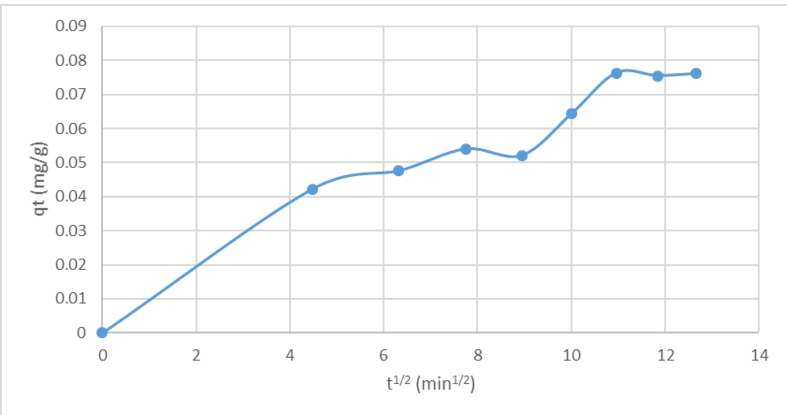


Figure 9 Intraparticle Diffusion Kinetic Model

Table 2 Kinetic Parameters

Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		$q_{e,exp}$ (mg/g)
$q_{e,cal}$ (mg/g)	K_1 (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	K_2 (g/mg min)	R^2	K_{diff} (mg g^{-1} $min^{-1/2}$)	R^2	
0.1683	0.0367	0.8517	0.0940	0.2675	0.9398	0.0047	0.9067	0.0763

The adsorption of Cr (VI) onto the hybrid sorbent as a multi-step process into the interior of sorbent as the plot in Figure 9 shows three intersecting lines. The first stage is the first sharper portion as the rapid external surface adsorption, the second linear portion with gradual adsorption as intraparticle diffusion and the final portion as the final equilibrium stage. The intraparticle diffusion step is the rate limiting factor and the final step came to equilibrium due to the very low metal ion concentration in solution phase and the limited available sorption sites on the biosorbent [6]. The kinetic parameters are also tabulated in Table 2.

3.10 Adsorption Isotherm Studies

The Langmuir, Freundlich and Temkin adsorption isotherm models were used to analyse the adsorption mechanism of Cr (VI) ions onto the hybrid eggshell-pandan sorbent surface. All the calculated parameter values are tabulated as in Table 3. For Langmuir isotherm, the R_L values lie between 0.3 and 0.8 for the initial Cr (VI) concentration range from 0.8 mg/L to 8 mg/L. This indicated that the adsorption is favourable as the values were in between 0 and 1 [24]. The n value in Freundlich isotherm model suggested the magnitude of ionic interactions of Cr (VI) ions and adsorbent [15]. The maximum adsorption capacity obtained from this model is 0.0453 mg/g. For Temkin isotherm, the B value indicated that the biosorption process happened in both chemisorption and physisorption [15].

Table 3 The Langmuir, Freudlich and Temkin parameters

Langmuir Isotherm	**b (L/mg)**	0.4189
	q_m (mg/g)	0.1712
	R_L	0.7490-0.2298
	R^2	0.9830
Freundlich Isotherm	**K_F [(mg/g)(L/mg)$^{(1/n)}$]**	0.0453
	n (g/L)	1.7790
	R^2	0.9988
Temkin Isotherm	**B (J/mol)**	0.0374
	A (L/g)	3.8895
	R^2	0.9747

From the Table 3, the value of R^2 showed that the experimental data were best fitted to the Freundlich isotherm model compared to that of Langmuir and Temkin isotherm with the values of 0.9988, 0.9830 and 0.9747 respectively. This suggests that the adsorption of Cr (VI) ions onto the hybrid eggshell-pandan sorbent is a multilayer adsorption. The surface of the hybrid sorbent is proven to be a heterogeneous surface, similar to the result in the adsorption kinetic studies. There are interactions between molecules attached onto the sorbent surface and the formation of monolayer is not restricted.

3.11 Thermodynamic Studies

To investigate the thermodynamic behaviour of the adsorption of chromium (VI) ions onto the hybrid eggshell-pandan sorbent, the thermodynamic parameters such as change in Gibbs free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) are determined. A graph of ln kd versus 1/T was plotted as in Figure 10. The change in enthalpy and change in entropy can be determined from the gradient and the intercept of the linear plot.

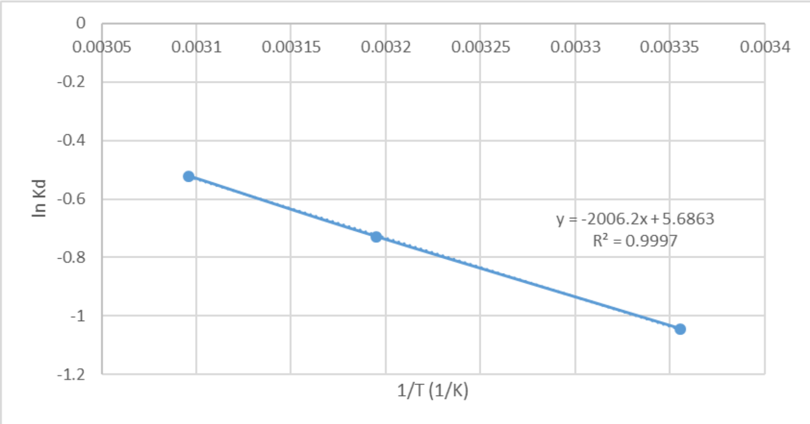


Figure 10 Thermodynamic Study

The calculated thermodynamic parameters are tabulated in Table 4. The Gibbs free energy values are all in negative. This indicates that the adsorption of Cr (VI) ions onto the hybrid eggshell-pandan sorbent is spontaneous and feasible throughout the experiment. Moreover, the positive value of the change in enthalpy implies that the adsorption process of Cr (VI) ions onto hybrid sorbent is endothermic and hence the process is more suitable to carry out in relatively higher temperature. Meanwhile, the positive value of ΔS° showed that the randomness at the solid solution interface increase [25].

Table 4 hermodynamic parameters

1/T (K^{-1})	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
0.0034	-2.5861	16.6796	0.0473
0.0032	-1.8954		
0.0031	-1.4005		

4.0 CONCLUSION

Hybrid eggshell-pandan sorbent was successfully synthesised in this study. The characterisation of hybrid sorbent and raw eggshell using FTIR proved the presence of O-H and N-H functional groups which are most probably responsible for the adsorption process. The SEM micrographs also indicated the attachment of 2-AP compounds onto the eggshell surface. BET analysis showed the decrement of specific surface area of the hybrid sorbent compared to the raw eggshell sorbent. The optimum conditions for the adsorption of chromium (VI) ions onto raw eggshell powder were 140 minutes contact time, 0.5 g dosage of biosorbent, 25°C and pH 5 of metal ions solution. While for hybrid eggshell-pandan sorbent, the removal efficiency were optimum when the contact time is 140 minutes, the dosage of hybrid sorbent is 0.5g and when the temperature is at 50°C and pH 4. Both type of biosorbents reach optimum efficiency at relatively low temperatures and acidic conditions, which proved them to be suitable being applied in industrial operations. Both biosorbents showed higher removal capacity but lower removal percentage at 0.8 mg/L of solution. Hybrid sorbent proved to be a better biosorbent as it had a higher removal percentage than raw eggshell in every parameters tested. The adsorption kinetic study indicated that the adsorption follows pseudo-second-order of Lagergren kinetic model with 0.94 R^2 value. Freundlich isotherm model which best fit with the experiment data proved the surface of the hybrid sorbent is heterogeneous. Biosorption of chromium (VI) ions by hybrid eggshell-pandan sorbent was spontaneous, feasible and an endothermic process. In short, the hybrid eggshell-pandan has potential as a marketable biosorbent.

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