



Adsorption efficiency of banana blossom peels (*musa acuminata colla*) adsorbent for chromium (VI) removal

M.A. Selimin^a, A.F.A. Latif^b, Y.C. Er^a, M.S. Muhamad^b, H. Basri^c, T.C. Lee^{a,*}

^a Faculty of Technology Management and Business, Universiti Tun Hussein Onn Malaysia (UTHM), 86400 Parit Raja, Johor, Malaysia

^b Faculty of Engineering Technology, UTHM, Pagoh Education Hub, 84600 Pagoh, Johor, Malaysia

^c Faculty of Applied Sciences and Technology, UTHM, Pagoh Education Hub, 84600 Pagoh, Johor, Malaysia

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ABSTRACT

The discharge of waste from industries into water has caused heavy metal pollution posing health risk to biota such as lead and chromium (VI). Once the water has been polluted, it will limit the accessibility to clean freshwater. Therefore, this paper aims to evaluate the adsorption efficiency of banana blossom peels for the chromium (Cr) (VI) removal under different pH (1, 4, 7, and 10). Extraction of banana blossom peels adsorbent was carried out via chemical treatment using 0.1 M of HCl and 5% (w/v) NaOH solution. The morphology and functional groups of extracted banana blossom peels adsorbent were then characterized using scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR), and subsequently, the Cr (VI) removal efficiency was examined using ultraviolet–visible spectroscopy (UV–VIS). The extracted banana blossom peels adsorbent is found to have wavy surface with shallow dents. Results demonstrated that adsorbent at pH 10 have the optimum removal of Cr (VI) with 18.87% followed by pH 7 (18.36%), pH 4 (12.28%) and pH 1 (12.00%) after 8 h. The maximum Cr (VI) adsorption capacity is 227.27 mg/g. In this study, the pseudo-second-order model best describes the adsorption process. Langmuir isotherm model is more favorable with high correlation coefficient of 0.99. In conclusion, adsorbent extracted from banana blossom has the potential to be used for Cr (VI) removal in water sources and reduce disposal of agricultural wastes by transforming it into a valuable material.

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1. Introduction

Recently, water crisis has become an environmental issue due to serious water pollution. The raise in water pollution rates is caused by human factors, discharge of wastes from industrialization, and agricultural activities. The discharge of wastes from industries into rivers has caused heavy metal pollution posing health risk to biota. Polluted water consequently limit accessibility to clean freshwater. According to Mekonnen and Hoekstra [1], up to 4 billions of the world's population is facing water scarcity at least one time annually and 1.6 billion people are experiencing economic water shortage. In Malaysia, for an example, the contamination of rivers has caused 744 times shutdown of the water treatment plants in Selangor from 2008 until 2019. According to Ang

[2], the river in Malaysia without pollution is declining from the year 2015 (58%) to 2017 (46%) while number of polluted water is rising gradually from year 2015 (35%) to 2017 (43%).

Chromium (VI) pollution is one of the serious environmental issues and challenges to the waterworks industry due to the hazardous substances of Cr (VI) that will cause harmful health effects. According to Moffat et al. [3], Cr (VI) has been determined as carcinogenic to humans as there is sufficient evidence to prove that lung cancer was caused by over-exposure to Cr (VI) in drinking water. High Cr (VI) intake through inhalation also leads to harmful effects on the kidney, respiratory tract, immune system, gastrointestinal, and liver. World Health Organization has set guidelines for the permissible limit of Cr (VI) contain in drinking water at 0.05 mg/L [4].

Some wastewater treatment technologies include wet air oxidation, supercritical oxidation, incineration, activated sludge, aerated lagoons, adsorption, stabilisation ponds, trickling filters, fixed-film

* Corresponding author.

E-mail address: tclee@uthm.edu.my (T.C. Lee).

reactors, and anaerobic degradation [5]. Among these, adsorption is an excellent alternative for Cr (VI) removal. Adsorption is a process that adhere ions or molecules (adsorbate) from a gas or liquid state to the surface of adsorbent. An adsorbent can be made from variety of waste materials including from natural agricultural wastes to remove Cr (VI) [6]. It is noteworthy to mention that the adsorption methods without using any toxic chemicals will not produce secondary effluents and it can be considered eco-friendly and cost-effective in removing Cr (VI). Furthermore, using agro-waste to produce adsorbent is more economical than the commercial activated carbon [7]. There are various methods of biological treatment for Cr (VI) using different agricultural waste materials such as pomelo peel, bamboo, tea leaf, nutshells, fish scales, fruit shells, eggshells, banana blossom peel etc [8–9].

Banana wastes including piths, fruit peels, pseudostems, banana leaves and banana blossoms are among the agricultural wastes that have potential against pollutant in aqueous solution [10]. According to Ku Ahmad et al. [11], banana is a fairly common crop in Malaysia, and its cultivation has covered around 26,000 ha of farmland, producing 530,000 metric tonnes yearly. Hence, banana wastes are abundantly available, low cost, easy to prepare and can be utilized as eco-friendly adsorbent in removing contamination and pollution in an aqueous solution. The presence of hydroxyl and carboxyl functional groups in banana-based adsorbent had been reported to be effective in removing heavy metal cations from the aqueous solution [12]. Whereas, the adsorption technique is among the crucial technique in various wastewater treatment processes compare to other techniques owing to its cost-effectiveness and ease of processing. There are several plant-based adsorbent extraction methods available, which can be clustered into four main groups; unmodified, physical, chemical and carbonization. Among these, chemical treatment can be considered as a simple and cost-effective method to extract the bioadsorbent [13–14].

To date, there is a lack of work reported on the extraction of plant-based adsorbents using banana blossom peels. Most of the work reported on the extraction from other parts of banana such as banana peels and their floret [15–16]. Studies on the effect of pH on Cr (VI) adsorption of banana blossom peels are still in their infancy. Hence, this study aims to extract bioadsorbent from banana blossom peels and investigate the Cr (VI) removal efficiency under different pH as pH is one of the crucial factors for metal ions adsorption in an aqueous solution [17]. In this study, the banana blossom peels adsorbent was extracted via chemical treatment in 0.1 M of HCl and 5% (w/v) NaOH solution for Cr (VI) removal [18]. In addition, the adsorption efficiency of extracted adsorbent was investigated under different Cr (VI) pH. It is expected that this study will provide significant contributions in wastewater treatment technology, ultimately improving quality of life and producing environmentally friendly solutions.

2. Experimental procedures

2.1. Banana blossom peels adsorbent extraction

In this study, banana blossom peels were obtained from grocery store at Parit Raja, Batu Pahat, Johor. Collected banana blossom peels were cut into small pieces using scissor. The banana blossom peels adsorbent extraction process was conducted by soaking and thoroughly washing the banana blossom peels in distilled water followed by air drying for 1 day to remove moisture. The banana blossom peels were then rinsed multiple times with distilled water after being treated with 0.1 M of HCl. Following that, a 5% (w/v) NaOH solution was employed to eliminate the residual crude proteins from banana blossom peels. Following the treatment process, the goods were continuously heated at 70 °C for 5 h before being

washed with distilled water and dried at 60 °C for 4 h. Subsequently, it was treated with 50% (w/v) NaOH solution and reheated at 100 °C with constant stirring for 1 h. Lastly, the banana blossom peels were thoroughly washed using deionized water until the washing solution reached neutral pH prior to drying at 60 °C in the oven. The extracted adsorbent was then shredded into fibre form using a blender.

2.2. Cr (VI) removal test

In 500 mL of distilled water, potassium dichromate ($K_2Cr_2O_7$) was used to prepare a Cr (VI) stock solution. 1.0 M HCl was added to the stock solution to get the acidic pH solution (pH 1 and 4). Meanwhile, an alkaline pH solution (pH 7 and 10) was obtained by utilizing 1.0 M NaOH. The batch adsorption experiments were carried out at different pH values of Cr (VI) solutions. Each adsorption experiment lasted 8 h, with an initial Cr (VI) concentration of 300 mg/L and adsorbent dosage of 0.25 g. The adsorbent was gently added, and the mixture was agitated at 170 rpm with a hot plate magnetic stirrer at room temperature.

Meanwhile, the concentration of Cr (VI) at 540 nm was measured using ultraviolet–visible spectroscopy (UV–VIS). Prior to the UV–VIS test, the concentration of Cr (VI) was determined using the diphenylcarbazide (DPC) technique [19] with a detection limit of 5 µg/L. In a volumetric flask, 1 mL of the sample was mixed with 0.2 mL of newly produced 0.25% (w/v) DPC (QRc) in acetone (Merck Schuchardt OHG) and 9 mL of 0.2 M H_2SO_4 (Merck Schuchardt OHG). To achieve full colour development (final process of DPC method), the mixture was vortexed for 15–30 s and left to stand for 10–15 min.

By using Eqs. (1) and (2), the quantity of Cr (VI) adsorbed per gram and the percentage of Cr (VI) removal by the banana blossom peels adsorbent were determined [20].

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (1)$$

$$\text{Adsorption (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where q_e (mg/g) represents the amount of metal ions, V represents the solution volume (L), W represents the adsorbent dose (g), C_0 (mg/l) denotes the initial Cr (IV) concentration and C_e (mg/L) denotes the equilibrium Cr (IV) concentration in solution.

2.3. Characterisation

Scanning electron microscopy (SEM) was used to investigate the morphologies of the extracted adsorbent. Fourier transform infrared spectroscopy (FTIR) was used to identified the structural properties of the adsorbent at wavelengths ranging from 400 to 4000 cm^{-1} .

3. Results and discussion

3.1. Surface morphology

Fig. 1 shows the SEM micrographs of banana blossom peels adsorbent at different magnifications. It can be noted that the surface morphology of banana blossom peels adsorbent shows shallow dents, irregular and wavy surface morphology with diameter around 1000 µm. At magnification of 5000X, wavy without pores and shallow dents morphology was observed. This is consistent with the findings of another study published by Omar et al. [18], which found that banana blossom peels have a wide surface area, irregular morphology, and highly porous structure, which led to

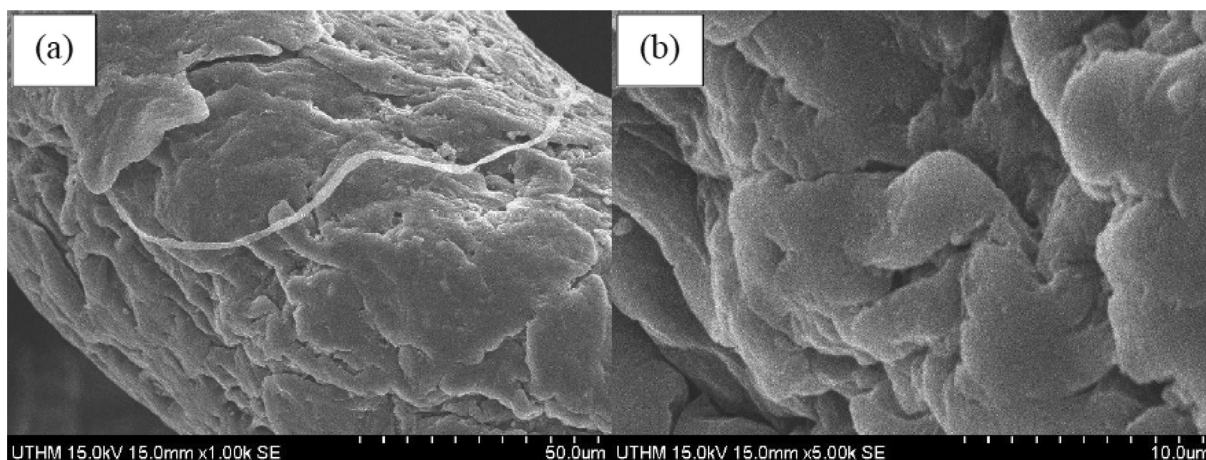


Fig. 1. Surface morphology of the initial banana blossom peels adsorbent, (a) 1000X and (b) 5000X.

an improvement in adsorption sites and adsorbent removal efficiency.

3.2. Structural characteristic

Functional groups of the adsorbent like hydroxyl and carboxyl groups play an important role for Cr (VI) removal. Fig. 2 shows the FTIR spectra of banana blossom peels adsorbent. The existence of significant hydroxyl (O-H) stretching vibration of cellulose molecules is related to the broad peak that appeared in the region of 3500 cm^{-1} to 3300 cm^{-1} [21–24]. Next, peak at 2920 cm^{-1} is characteristic of C-H stretching. Meanwhile, presence of O-H bending of adsorbed water was proved by the band at 1616 cm^{-1} . The existence of C-H bending and O-H bending vibrations was represented by vibrational peaks at 1311 cm^{-1} and 1375 cm^{-1} , respectively. C-O stretching is linked with the band at 1244 cm^{-1} , whereas alcohol C-O stretching is associated with the narrow shoulder peak at 1028 cm^{-1} . Furthermore, the tiny peak at 961 cm^{-1} is owing to the existence of D-glucose molecule, whereas the band at 895 cm^{-1} is related to the presence of β -glycosidic linkages between monosaccharides.

The FTIR results are consistent with findings by Omar et al. [18] which studied the manganese removal efficiency of banana blossom peel and floret. Both previous and current studies showed the appearance of similar adsorption bands in similar wavelength ranges and explained that the hydroxyl and carboxyl groups of banana blossom adsorbent, as these groups will give a significant influence on the Cr (VI) removal efficiency [12,15]. Basically, Cr (VI) has several oxyanion forms. Chromic acid (HCrO_4^-) is a predominant Cr (VI) oxyanion and has a strong negative charged anion in acidic conditions. Meanwhile, in alkaline conditions, Cr (VI) oxyanions such as chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) appeared to be a predominant species [25]. Both hydroxyl and carboxyl groups of banana blossom peel adsorbent will give significant effect toward the Cr (VI) removal effectiveness either in acidic or alkaline conditions.

3.3. Cr (VI) removal rate

As demonstrated in Fig. 3, the first 2 h of contact time of the Cr (VI) solution with banana blossom peels adsorbent results in a modest reduction of Cr (VI) concentration for all pH values of Cr

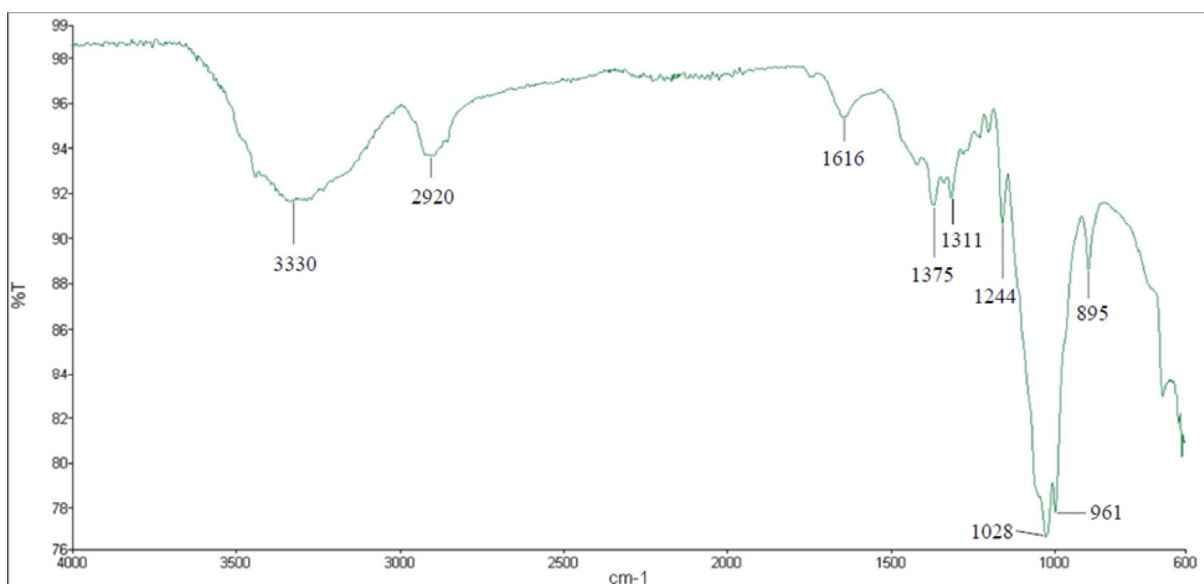


Fig. 2. FTIR spectrum of banana blossom peels adsorbent.

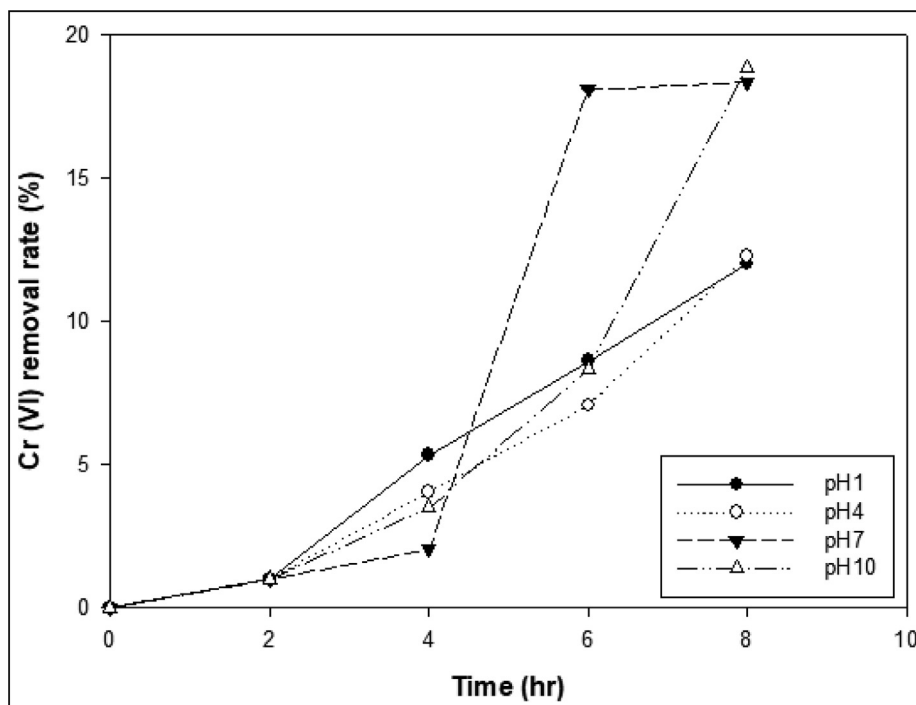


Fig. 3. Removal efficiency of Cr (VI) at different pH.

(VI) concentration. Further elimination of Cr (VI) was seen after 4 h of contact time with adsorbent at pH 1. This adsorbent had the greatest removal efficiency of 5.33% when compared to other adsorbent at different pH values. After 6 h of contact time, adsorbent at pH 7 displays better removal of Cr (VI), which is 18.09% followed by pH 1, pH 10 and pH 4. Increased contact duration to 8 h resulted in a very substantial effect on Cr (VI) removal for all adsorbents except adsorbent at pH 7.

After 8 h, the greatest Cr (VI) removal rate was recorded at pH 10 with 18.87% (243.39 mg/L from an initial concentration of 300 mg/L). Besides that, the adsorption experiment at pH 7 showed highest Cr (VI) removal rate after 6 h of contact time compared to pH 1, 4 and 10. As evident, adsorption was slightly enhanced by increasing the pH to alkaline level. Therefore, pH was considered as one of the significant parameters in adsorption process which

brought impact on surface change. In this study, the banana blossom peels more favored in alkaline condition.

The main ions that appeared in acidic Cr (VI) is acid chromate (H_2CrO_4) while the main ions that appeared in alkaline Cr (VI) is dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and chromate (CrO_4^{2-}) [26]. The Cr (VI) removal efficiency was related to the surface functional groups of banana blossom adsorbent. The functional groups of banana blossom adsorbent that integrates with dominant species of Cr (VI) in aqueous solution could contribute to adsorption process and promote higher Cr (VI) removal efficiency at alkaline pH. The optimal Cr (VI) removal at pH 10 could be associated with enhanced positively charged functional groups of banana blossom adsorbent and the chemical exchange at alkaline level. The hydroxyl functional group are able to bind to metal ions by substituting hydrogen ions with metal ions in solution [27].

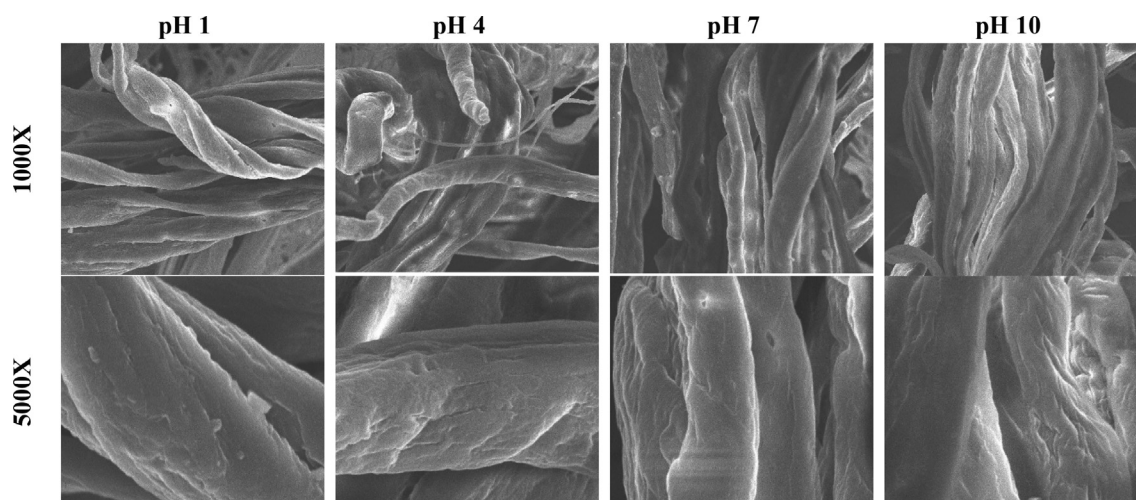


Fig. 4. Surface morphology of banana blossom adsorbent peels after the Cr (VI) removal test at different pH.

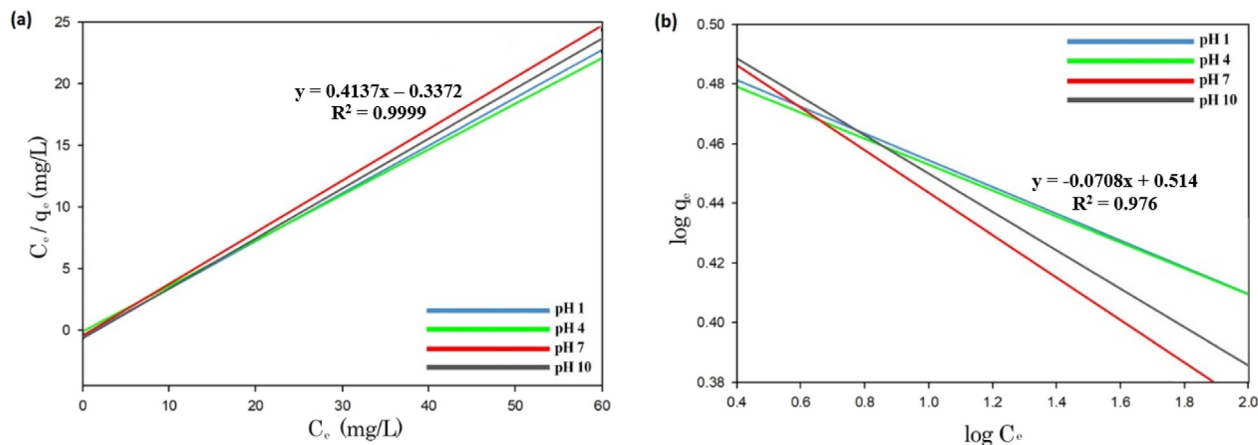


Fig. 5. Adsorption of Cr (VI) by (a) Langmuir and (b) Freundlich isotherm model.

Table 1
Langmuir and Freundlich constants and correlation coefficients for adsorption of Cr (VI).

| Langmuir | | | | Freundlich | | |
|------------|--------|--------|--------|------------|--------|-------|
| q_{\max} | b | R^2 | R_L | K_F | $1/n$ | R^2 |
| 2.417 | 1.2269 | 0.9999 | 0.0027 | 0.6655 | 0.0708 | 0.976 |

In contrast to Mondal et al. [28], banana peel dust (BPD) has a greater Cr (VI) removal rate (91.80% at 100 mg/L) and a different optimal pH for adsorption capacity than banana blossom peels adsorbent extracted in this work, which has a maximum Cr (VI) removal rate of 18.87% at 300 mg/L. The optimal pH for BPD is acidic (pH 1), whereas the optimal pH for banana blossom peels is alkaline (pH 10). Furthermore, Rahim and Haris [29] study found that banana trunk fibres reinforced chitosan (BTF-i-CTS) had a better efficiency to remove chromium (VI) due to a shorter contact period (120 min) to reach up to 97.79% removal rate at an initial concentration of 50 mg/L.

Fig. 4 shows the surface morphologies of banana blossom peels adsorbent after adsorption at different pH and magnifications. It can be noted that the morphologies exhibit smooth but with many vacuoles observed in acidic pH 1 of Cr (VI) solution. Diameter of the adsorbent also reduced to about 120 μm . Meanwhile in pH 4, the adsorbent diameter is around 100 μm and perceptibly smaller than adsorbent in pH 1. The fibrils are slightly adhered to each other and presented more rod-like structure of the banana blossom peels

adsorbent after adsorption at pH 4 and above. Further increment on Cr (VI) initial concentration at pH 7 formed tight adhesion between fibrils without any lumen. The morphology of adsorbent at pH 10 indicates that the fibrils are moderately adhered to each other and emerging rope-like structure without any lumen.

3.4. Isotherm adsorption

The sorption capacity of the adsorbent is defined by using the most commonly used isotherm models, Langmuir and Freundlich [30]. The Langmuir adsorption isotherm assumed the monolayer adsorption on the surface of adsorbent. Meanwhile, Freundlich isotherm is valid if the heterogeneous system acting on the surface of adsorbent [31]. It is obtained that the maximum adsorption capacity, q_{\max} for Cr (VI) is 2.42 mg/g. The Langmuir isotherm is favourable since the obtained R_L lies between 0 and 1 [32]. Further, the Freundlich affinity constant (K_F) was found to be 0.655. The heterogeneity parameter ($1/n$) is 0.078 verifies that the adsorption condition was favourable [33]. The corresponding Langmuir and

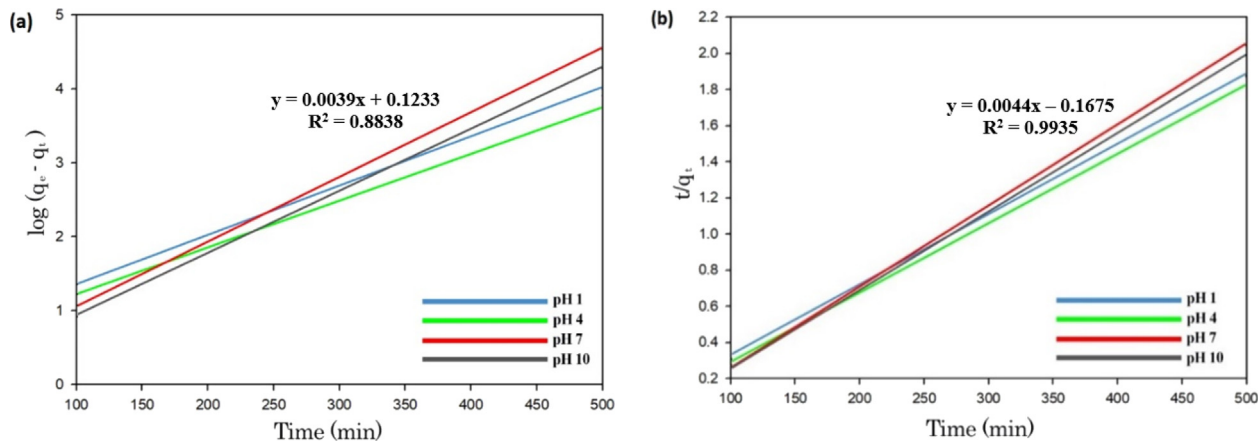


Fig. 6. Linearized plot of experimental data using (a) pseudo-first order model and (b) pseudo-second order model.

Table 2

Parameters of pseudo-first order and pseudo-second order models.

| Pseudo-First Order | | | Pseudo-Second Order | | |
|--------------------|--------|--------|---------------------|--------|--------|
| q_e | K_1 | R^2 | q_e | K_2 | R^2 |
| 2.0931 | 0.0089 | 0.8838 | 227.27 | 0.0263 | 0.9935 |

Freundlich isotherms plots are shown in Fig. 5, meanwhile Table 1 shows the parameters of the both models. In this study, Langmuir isotherm shows greater suitability with high correlation coefficients of 0.99. The greater suitability of the Langmuir isotherm suggests that the adsorption of Cr (VI) onto banana blossom peels adsorbent occurred with the formation of a monolayer, and the force observed between the adsorbent and the adsorbate is the result of physical interaction, as is typical in heavy metal removal using natural adsorbent. Several experts have reported similar findings in the removal of heavy metals such as plumbum [34].

3.5. Kinetic adsorption

In this study, the mechanism of kinetic adsorption is identified by using kinetic models which are pseudo-first-order and pseudo-second-order model. Pseudo-first-order is used for the liquid/solid system in which the rates of change are proportional to the remaining amount of surface sites. Meanwhile pseudo-second-order model is valid when the rate is proportional to the square surface sites [35]. The linearized plots of both models are shown in Fig. 6. K_1 , K_2 and q_e are calculated from the slopes and listed in Table 2. With higher value of correlation coefficient, Pseudo-second-order model fits better for adsorption kinetics of Cr (VI). It is found that the maximum Cr (VI) ion adsorbed, q_e is 227.27 mg/g. The adsorbent shows high adsorption capacity for Cr (VI) which was recorded in several studies; 104 mg/g [36], 374.53 mg/g [37], and 417.19 mg/g [38].

4. Conclusions

This study investigated the adsorption efficiency of banana blossom peels extracted adsorbent for Cr (VI) removal. Banana blossom peels adsorbent showed wavy, shallow dents, rocky and irregular morphology with diameter for initial and after Cr (VI) removal test were 1000 μ m and 100–150 μ m, respectively. The FTIR spectrum of banana blossom peels adsorbent showed that this adsorbent exhibit strong hydroxyl (O-H) stretching vibration of cellulose molecules, C-H stretching, O-H bending of adsorbed water, C-H bending, and O-H bending vibrations, C-O stretching, D-glucose compound, and β -glycosidic linkages between monosaccharides. These are the critical hydroxyl and carboxyl functional groups for heavy metal pollutant adsorption effectiveness in aqueous solution. The UV–VIS results showed that banana blossom peels adsorbents achieved the highest Cr (VI) removal rate of 18.87% at pH 10 after 8 h of contact time. Pseudo-second-order model and Langmuir isotherm model best describe the adsorption process occurred in this study with high correlation coefficient of 0.99. Hence, banana blossom peels adsorbent exhibits reasonably good adsorbent characteristic for the removal of Cr (VI) in water and can be fully utilized instead of discarding as waste material.

CRedit authorship contribution statement

M.A. Selimin: Writing – original draft, Formal analysis. **A.F.A. Latif:** Writing – original draft, Visualization, Investigation. **Y.C. Er:** Investigation. **M.S. Muhamad:** Writing – review & editing, Funding acquisition, Validation. **H. Basri:** Writing – review & edit-

ing, Validation. **T.C. Lee:** Conceptualization, Methodology, Supervision, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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