



## Adsorption studies on heavy metal removal from synthetic wastewater by pyrolyzed chicken feather fiber

Wei Chek Moon, Puganeshwary Palaniandy\*, Mohd Suffian Yusoff, Irvan Dahlan

School of Civil Engineering & School of Chemical Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia, Tel. +604-5995883; email: cepuganeshwary@usm.my (P. Palaniandy), Tel. +6016-5633046; email: vmoonpower@yahoo.com.my (W.C. Moon), Tel. +604-5996223; email: suffian@usm.my (M.S. Yusoff), Tel. +604-5996463; email: chirvan@usm.my (I. Dahlan)

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### ABSTRACT

In this study, chicken feather fiber was treated by a two-step pyrolysis and tested as an adsorbent to remove calcium, manganese and copper from synthetic wastewater. Batch adsorption studies were performed to investigate the effect of pH (3–5) and mass of adsorbent (0.2–1.5 g). Experimental results revealed that the optimum conditions for all three metals removal were at pH 4.89 and 1.5 g of adsorbent with the highest percentage removal of 21% for the copper. From ANOVA analysis, mass of adsorbent was found to be the most influential factor for the removal of heavy metal in this study. The adsorption isotherm for copper removal was suitably described by Langmuir equation with the maximum adsorption capacity of 2.0829 mg/g. The unsatisfactory removal may be attributed to the melting of keratin during the fast heating rate (30°C) used in this study. The results from this experimental work have provided useful information on the characteristics of thermal treatment on the chicken feather (CF) and can be used as a preliminary data for researchers to study the PCFF as a low-cost adsorbent.

*Keywords:* Chicken feather; Pyrolysis; Calcium; Manganese; Copper

### 1. Introduction

Nowadays, the rapid industrialization of human society has caused the accumulation of heavy metal in wastewater. Due to more stringent regulations, heavy metals are the priority pollutants and are becoming one of the most serious environmental problems nowadays [1]. Heavy metals are individual metals and metal compounds which cause varying degrees of illness based on their acute and chronic exposures [2]. Unlike organic pollutants, heavy metals present in the industrial effluents remain as alarming pollutants due to their non-destructive nature, toxicity, bioaccumulation and subsequent biomagnifications [3]. The main threats to human health from heavy metals are associated with exposure to arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver.

Adsorption process is one the widely used methods to deal with the wastewater treatment when the metal concentrations are in the range of 1–100 mg/L [4]. Through the years, the development of low-cost adsorbents had been an attempt for the worldwide researchers instead of using high-cost adsorbents [5]. Recently, worldwide poultry consumption has generated a huge amount of chicken feather (CF) annually [6]. In fact, studies have shown the fibrous proteins contained in some wastes from the animal processing industry are abundant resources for obtaining the sorbents for wastewater treatment [4,7,8]. Despite the beneficial reuse of the CF, most of them are still treated as waste product currently [9]. There are two activation methods by thermal and chemical treatment of chicken feather fiber (CFF) to enhance their structural changes for a better adsorption [10]. However, most of the studies focus on CFF by chemical activation.

Chemically treated CF has been studied and used widely in the treatment of wastewater which contains the polluting metals from industrial water [3,4,8,11–13]. The treated metal

\* Corresponding author.

ions include copper, zinc, calcium, magnesium, iron, manganese, lead, cadmium and nickel. Based on their batch studies, the concentration of heavy metal, the mass of CF, the pH value and the temperature are the common influential factors for the removal efficiency of heavy metal. Results have shown that CF is found convincing to be used as a low-cost sorbent for the removal of heavy metal. Besides, the ability of chemically treated CF also has been studied in the dye removal [7,14–16]. Four types of dyes have been treated such as Malachite Green, Brilliant Blue FCF, Tartrazine and Indigo Carmine. Furthermore, CF has been used as spill clean-up sorbent in the oil industry. The removal of petroleum hydrocarbons is studied in a keratinolytic mixed culture which is a system containing keratinous chicken feathers at different concentrations of petroleum hydrocarbons [17].

Recently, the thermal treatment or known as pyrolysis had been introduced [18]. The characteristics of CF after two-step pyrolysis process have been explored by Senoz and Wool [19] for hydrogen storage purpose. A two-step pyrolysis method enhances the porous nature of CFF and its quality with high temperature resistive [10]. Results have shown that the pyrolyzed chicken feather fibers (PCFF) demonstrate a strong  $H_2$  adsorption affinity at low pressures and 77 K due to the microporous nature of PCFF. Therefore, this study focuses on the capability of PCFF in the removal of heavy metal ions from synthetic wastewater.

This study not only aimed to investigate the characteristics of PCFF, but also evaluating its adsorption performance by synthesizing, measuring and analyzing the removal efficiency of polluting metals in the synthetic wastewater. This was followed by the optimization process of the operating factors to obtain the highest heavy metal removal by using the chosen PCFF. Lastly, the process of adsorption was described through the determination of adsorption isotherm value.

## 2. Materials and methods

### 2.1. Cleaning and preparation of CFF

Raw CF was collected from Ayamplus Food Corporation Sdn Bhd. The preparation of CFF as an adsorbent was carried out according to the method described by Gassner III et al. [20] with some modifications. There are five basic steps in the

preparation of CFF, namely, collecting, washing, repeating, drying and removing [20]. In this study, the first step was the collecting and washing of the raw CF with water. This was followed by the removal of CFF from the feather shaft. The CF was then washed with ethanol 95% for 1 h to remove the oil, fats and partially dehydrate the feathers. For a good agitation, the mixing ratio of 0.5 L from ethanol to 6 g of CF was used in the washing step. After that, the washing step was repeated by using ethanol 70% to further sterilize the feather from bacteria. Finally, the CFF were dried at 60°C for 24 h and stored for further use.

### 2.2. Thermal treatment

According to Senoz and Wool [10], a two-step pyrolysis method was used to enhance the quality of CFF to high temperature resistive and a good adsorbent with high surface area and degree of porosity. In this study, PCFF was pyrolyzed in a fixed bed reactor which was constructed from a 60 × 6.9 cm ID 310 stainless steel tube and centrally positioned within an enclosing Carbolated VST vertical tubular electric furnace. Before the pyrolysis process started, a constant flow of  $N_2$  was provided for 0.5 h to minimize the oxygen concentration. The general temperature profiles with respect to time in two-step pyrolysis are illustrated in Fig. 1. Two samples of PCFF with different heating temperature as shown in Table 1 were prepared in the experiment. After completing the two-step pyrolysis, PCFF samples were cooled in the tube furnace at below 100°C under nitrogen gas for 3 h. Then, the PCFF samples were washed with 100 mL of toluene and 300 mL of distilled water to remove the impurities, then

Table 1  
Different pyrolysis conditions for the experiment

Sample	PCFF-1	PCFF-2
$T_1$ (°C)	215	185
$t_1$ (h)	5	5
$T_2$ (°C)	400	400
$t_2$ (h)	1	1
$r_1, r_2$ (°C)	30	30

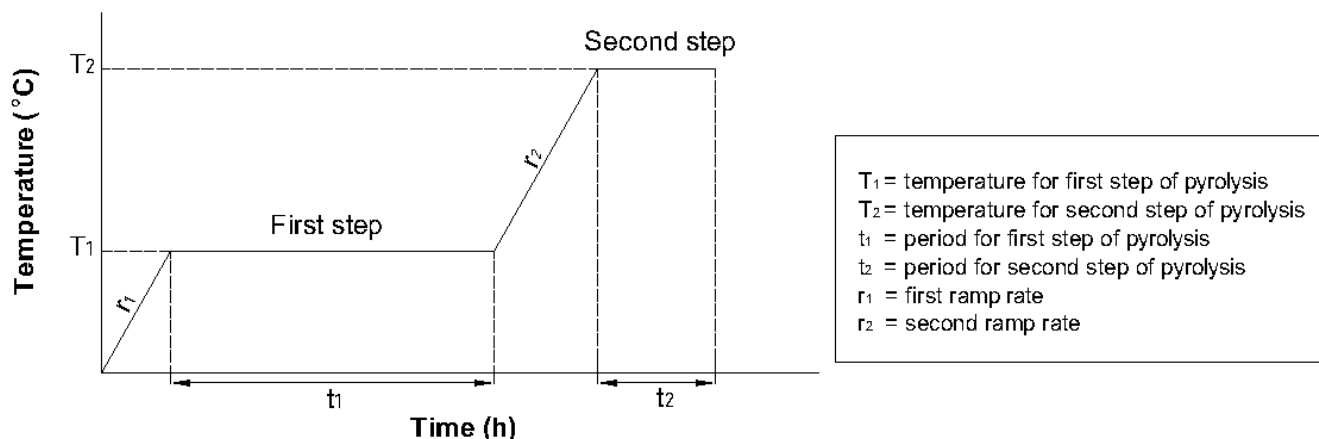


Fig. 1. General temperature profiles with respect to time in two-step pyrolysis.

followed by drying in an oven at 60°C overnight for later use in the adsorption experiment. Information on the morphological shape of the PCFF was observed by scanning electron microscopy (SEM) using a Zeiss Supra 35VP scanning electron microscope.

2.3. Batch adsorption study

All chemicals used for the preparation of synthetic wastewater were of analytical grade: calcium chloride (CaCl<sub>2</sub>·2H<sub>2</sub>O), manganese sulfate (MnSO<sub>4</sub>·H<sub>2</sub>O) and copper chloride (CuCl<sub>2</sub>·2H<sub>2</sub>O). Adsorption process was conducted at room temperature with a constant shaking time of 1 h and shaking rate of 150 rpm. Heavy metal analysis was carried out by using Varian 715-ES Inductive Couple Plasma (ICP) optical emission spectrometer. Besides heavy metal analysis, pH of the treated samples was checked by using Hanna HI 8424 pH meter.

Batch adsorption studies were performed using 100 mL of synthetic wastewater at concentrations of 50 mg/L to study the effect of pH and mass of adsorbent varying from 3 to 5 and from 0.2 to 1.5 g, respectively on the removal of calcium, manganese and copper. The pH value plays an important factor as it causes the ionization of actives sites on CF and affects its removal efficiency [13]. The experimental design was done using central composite design (CCD) in Design Expert software version 6.0.6. For this experiment, a total of 13 runs were conducted, as shown in Table 2. In the optimization process, numerical optimization was used to determine the optimum conditions for the maximum removal of heavy metals.

2.4. Adsorption isotherm study

The adsorption isotherm values were determined by using different initial concentrations of the chosen heavy metal. The isotherm study was conducted at room temperature. The experiment was carried out by shaking the synthetic solution samples containing the heavy metal concentrations varying from 10 to 50 mg/L, with the optimum amount of PCFF and pH (obtained in the optimization process) within

1 h shaking time to ensure the attainment of equilibrium. In this study, the popular models, namely Langmuir and Freundlich isotherms were used to describe the characteristics of adsorption. The linear form of the Langmuir and Freundlich isotherms are defined as shown in Eqs. (1) and (2). The applicability of the isotherms was compared by judging the coefficient of determination (R<sup>2</sup>).

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o} \tag{1}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{2}$$

where C<sub>e</sub> (mg/L) is the final concentration of adsorbate, q<sub>e</sub> (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, Q<sub>o</sub> (mg/g) is the empirical Langmuir constant related to maximum adsorption capacity, b (L/mg) is the empirical Langmuir constant related to rate of adsorption, K<sub>f</sub> (mg/g) is the empirical Freundlich constant or capacity factor, 1/n is the Freundlich intensity parameter.

3. Results and discussions

3.1. Pyrolysis process

Table 3 shows the pyrolysis parameters with the physical appearance and the residue fraction of the final PCFF products. No significant difference in physical appearance was observed between PCFF-1 and PCFF-2. Fig. 2 shows the appearance of CFF before and after the pyrolysis process. An isothermal heat treatment at 215°C or less was able to avoid the CF from partial melting and to maintain the original CFF structure intact [10]. However, both the structures of PCFF-1 and PCFF-2 were not intact in this study. During pyrolysis, the fibrous structure of CFF should be retained. The differential physical appearance may be related with the fast heating rate (30°C/min) applied in this study. Senoz et al. [21] stated that during rapid heating (50°C/min), the fibrous structure of CFF was collapsed into completely melted residues as the disulfide bonds were broken and there was insufficient time for the crosslinking reactions.

The information on the morphological shape of the PCFF-1 and PCFF-2 is shown in Fig. 3. No obvious porosity in both PCFF was being detected by SEM. It can be observed that the surface of PCFF-1 was smoother whereas the surface of PCFF-2 was rougher. According to Senoz and Wool’s findings, the surface of PCFF-1 should be microporous instead of smooth. The smooth surface of PCFF-1 in this study can be due to the melting of the CFF structure during the first step of pyrolysis or known as isothermal heat treatment. The first step of heat treatment below the melting point of CFF

Table 2  
Experimental design

Run	pH	Mass of adsorbent (g)
1	3	0.85
2	3	0.2
3	3	1.5
4	4	0.85
5	4	0.85
6	5	0.85
7	4	1.5
8	5	1.5
9	5	0.2
10	4	0.85
11	4	0.85
12	4	0.85
13	4	0.2

Table 3  
Pyrolysis parameters of the final PCFF products

Sample	Physical appearance	Residue fraction
PCFF-1	Shiny black, not intact	0.4962
PCFF-2	Shiny black, not intact	0.5028

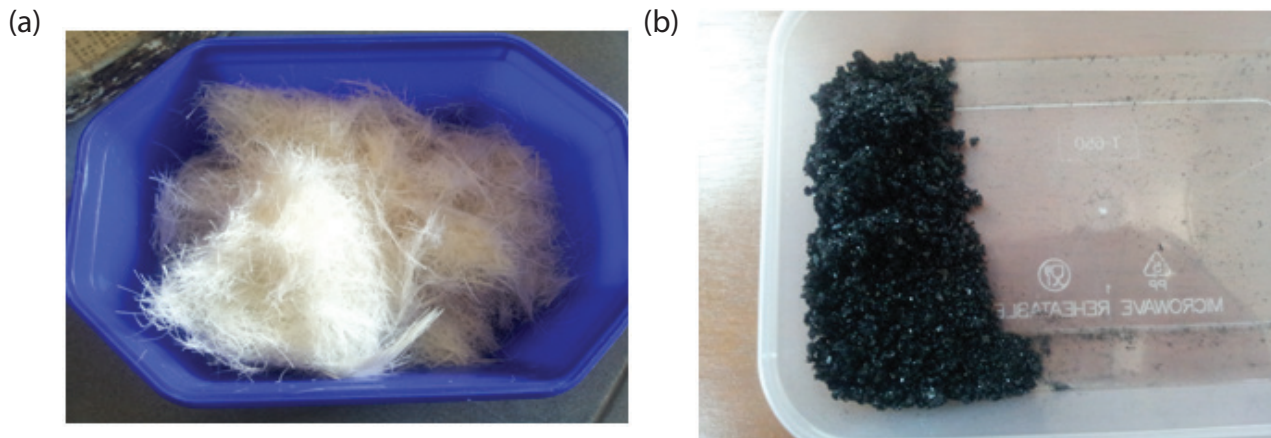


Fig. 2. Chicken feather fibers (a) before and (b) after pyrolysis.

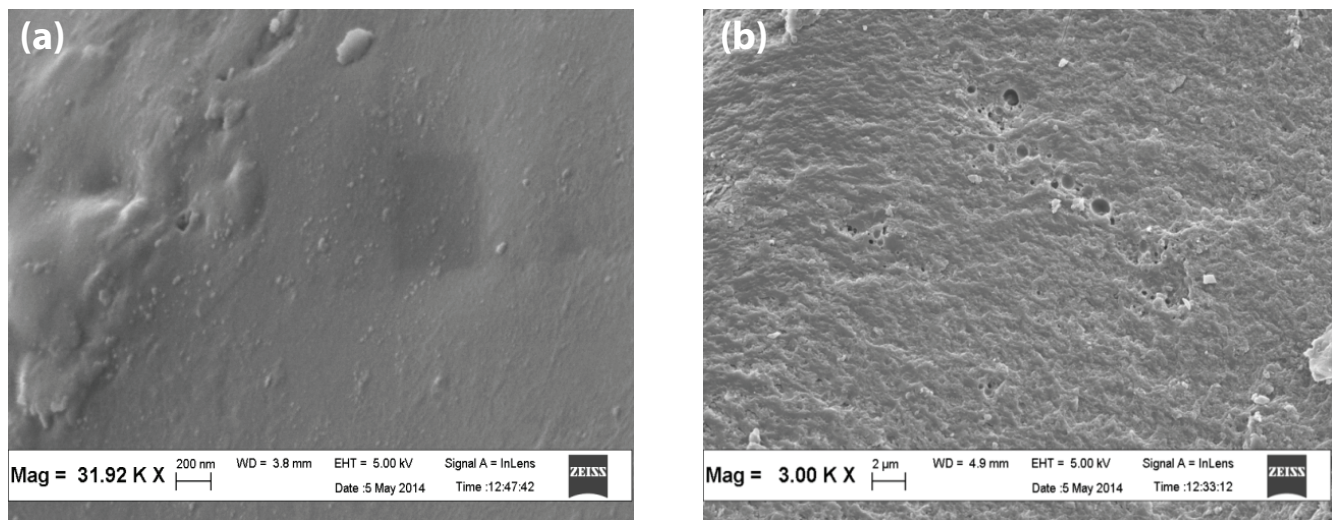


Fig. 3. PCFF-1 (a) and PCFF-2 (b) in SEM investigations.

(215°C) is a critical step for the preparation of fibers at higher temperatures [19]. As the temperature of heat treatment for PCFF-1 is set at 215°C, there is a possibility that the actual temperature goes beyond the temperature that had been set.

### 3.2. Batch adsorption study

In this study, the removal of heavy metal ions (calcium (Ca), manganese (Mn) and copper (Cu)) was evaluated by using PCFF-2. It is because that a preliminary study was done on the adsorption using two PCFF's and PCFF-2 was showing better removal performance as compared to PCFF-1 (results on this part are not discussed). The results of removal percentage are shown in Fig. 4. As shown in Fig. 4, the removal efficiency ranged from 3.83% to 10.95% for calcium, 4.09% to 11.44% for manganese and 5.86% to 20.66% for copper. As comparing their respective particle sizes, it indicated that the smaller particle size of heavy metal resulted in a better removal efficiency of heavy metal by PCFF. However, the results showed unsatisfactory removal performance. In this study, a heating

rate of 30°C/min was applied in the pyrolysis process due to the limitation of the equipment. This can be explained by the melting of keratin during the fast heating rate, simultaneously affecting the reactive sites towards metal uptake [4].

As for the pH of the treated samples, the results in Fig. 5 showed that the pH increased slightly after the treatment process for each run of the experiment. In fact, the positive ions contributed to the acidic condition in wastewater [22]. Therefore, the increased pH after the treatment process can be explained that some of the metal ions which carried the positive charges have been adsorbed onto the surface of PCFF.

#### 3.2.1. ANOVA

Based on the experimental results from the CCD design, graphical analyses were carried out to determine the interactions between the variables and the responses in the experiment. The ANOVA results of the models for calcium ( $Y_1$ ), manganese ( $Y_2$ ) and copper ( $Y_3$ ) removal are presented in Table 4. For the removal percentage of manganese and

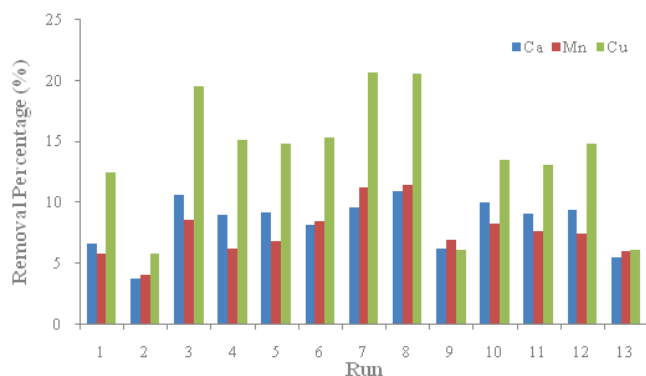


Fig. 4. Response values based on the experimental runs.

copper, the linear model was selected as suggested whereas the quadratic model was selected for the percentage removal of calcium. Based on Table 4, the  $R^2$  values obtained in the present study for  $Y_1$ ,  $Y_2$  and  $Y_3$  were 0.9095, 0.8860 and 0.9711, respectively. Generally, the  $R^2$  value which is approaching 1 indicates a good agreement between the outcomes and their predicted values. Same concept goes to standard deviation. The smaller is the standard deviation, the better is the model. In addition, the adequate precision (AP) for the models  $Y_1$ ,  $Y_2$  and  $Y_3$  were 12.764, 20.493 and 34.062, respectively. As the value of AP is above than 4, it indicates an adequate signal. Thus, the AP values for all three models were desirable.

Moreover, the adequacy of the models can be further justified by the  $F$ -value. In Table 4, the  $F$ -values of 14.07, 38.85 and 167.87 for  $Y_1$ ,  $Y_2$  and  $Y_3$ , respectively showed that the models were significant. Besides, the values of  $\text{Prob} > F$  which are less than 0.05 indicate the model terms are significant. On the other hand, values greater than 0.1 indicate the model terms are not significant. Based on Table 5, the models  $Y_1$ ,  $Y_2$  and  $Y_3$  were significant due to their  $\text{Prob} > F$  were less than 0.05. Mass of adsorbent appeared to be the most influential factor for the removal of heavy metal in this study. This can be seen clearly in Table 4, the factor B, referring to the mass of adsorbent was significant with the value of  $\text{Prob} > F$  of 0.0001 for the three models.

Model adequacy can also be judged by applying diagnostic plots which were provided by the Design- Expect 6.0.6. Fig. 6 illustrates the plots of predicted values vs. experimental values for (a) calcium, (b) manganese and (c) copper. As shown in Fig. 6, the data points (actual values) almost fell along the straight line (predicted values) although there was some scattering for the plots of calcium and manganese. However, most of the actual values were close to the predicted values. It showed that it was in agreement with the results from the statistical analysis.

The 3D surface response and contour plots of the models which were obtained from the Design-Expect 6.0.6 show the interactive relationship between the independent variables and the responses (Fig. 7). Based on Fig. 7(a), the highest removal percentage for calcium was as much as 11%, with the optimum conditions of pH 4 and the mass of adsorbent of 1.5 g. From Fig. 7(b), manganese removal is optimum which was approximately 11% at the pH 5 and mass of adsorbent of 1.5 g. As shown in Fig. 7(c), the removal percentage for copper reaches a maximum at around 21% when the pH and mass of adsorbent are 5 and 1.5 g, respectively.

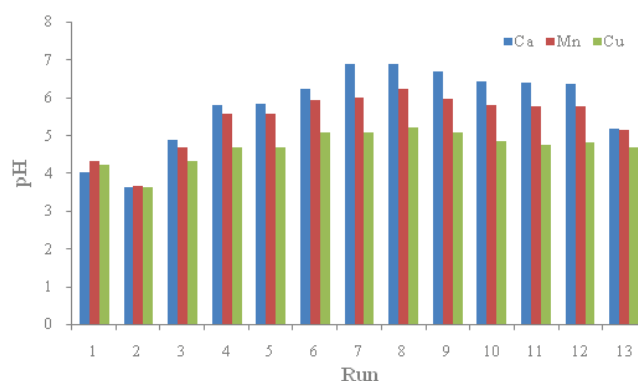


Fig. 5. pH value of the treated samples.

In the study, first-step pyrolysis was conducted below the melting point of keratin (215°C). The aim of the first-step pyrolysis is important in controlling the physical properties and thermal stability of the final product [21], so that the fibrous structure of CFF is able to be stabilized and strengthened before subjected to the second-step pyrolysis with higher temperature. The PCFF obtained from second-step pyrolysis is believed to perform better in term of mechanical properties as a high amount of crosslinked keratin is modified: a carbon-nitrogen fiber with oxygen functionalities supported by aromatic groups and double as well as triple bonds.

Here, a heating rate of 30°C applied in this study was found to cause the broken of disulfide bonds and provide insufficient time for the crosslinking reactions such as isopeptide formation. The crosslinked structure is important to provide extra support to the CFF from the melting transition, simultaneously contributing to a more stable structural material for further heat treatment. In the end, the final product of PCFF resulted in a congealed block of melted protein instead of a microporous material and consequently reducing the reactive sites of keratin which have a natural affinity toward metals. Therefore, little sorption was observed for all three type of heavy metals in this study.

However, from previous studies, the CF that has been treated chemically to remove Ca, Mn and Cu from wastewater showed a good removal [11,12]. Based on the study carried out by Al-Asheh et al. [11], the treated CF performed high efficiency to remove Cu three times greater than the untreated CF, which was around 83% of removal. Here, the treatment with alkaline solution has led to the increase of the softness of the CF, simultaneously increasing the metal uptake. During the treatment with NaOH, the decrease in the cross-linkage of the keratin fibers made the functional groups to be more accessible at the surface rather than the pores of CF only.

On the other hand, Sayed and his co-researchers also proposed the use of CF after the alkaline treatment with NaOH, but together with the immobilization of the produced hydrolyzates on silica surface as sorbent to remove Ca and Mn from the industrial water. Results have shown that the Ca and Mn removal efficiency was increased up to 93.38% and 95.66%, respectively. Therefore, the alkaline treatment was playing an important role in yielding the active amino acid residues due to the decrease in the cross-linkage of keratin and the enhancement of the hydrolysis rate of the peptide bonds [12].

Table 4  
ANOVA results of the model for  $Y_1$ ,  $Y_2$  and  $Y_3$

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model ( $Y_1$ )	49.52	5	9.90	14.07	0.0016
A	3.18	1	3.18	4.52	0.0711
B	40.20	1	40.20	57.10	0.0001
A <sup>2</sup>	1.93	1	1.93	2.74	0.1418
B <sup>2</sup>	1.19	1	1.19	1.69	0.2352
AB	1.14	1	1.14	1.63	0.2429
Residual	4.93	7	0.70		
Pure Error	0.61	4	0.15		
Cor Total	54.45	12			
Std. Dev., 0.84; Mean, 8.35; C.V., 10.05; PRESS, 33.44; R-Squared, 0.9095; Adj R-Squared, 0.8448; Pred R-Squared, 0.3857; Adeq Precision, 12.764.					
Model ( $Y_2$ )	45.18	2	22.59	< 0.0001	< 0.0001
A	11.48	1	11.48	< 0.0001	0.0012
B	33.70	1	33.70	< 0.0001	< 0.0001
Residual	5.81	10	0.58	< 0.0001	
Pure Error	2.50	4	0.63	< 0.0001	
Cor Total	51.00	12		< 0.0001	
Std. Dev., 0.76; Mean, 7.64; C.V., 9.98; PRESS, 8.58; R-Squared, 0.8860; Adj R-Squared, 0.8632; Pred R-Squared, 0.8318; Adeq Precision, 20.493.					
Model ( $Y_3$ )	306.86	2	153.43	167.87	< 0.0001
A	2.98	1	2.98	3.26	0.1010
B	303.88	1	303.88	332.47	< 0.0001
Residual	9.14	10	0.91		
Pure Error	3.26	4	0.81		
Cor Total	316.00	12			
Std. Dev., 0.96; Mean, 13.73; C.V., 6.96; PRESS, 16.17; R-Squared, 0.9711; Adj R-Squared, 0.9653; Pred R-Squared, 0.9488; Adeq Precision, 34.062.					

Table 5  
Optimum conditions for the maximum removal of heavy metal

pH	Mass of adsorbent (g)	Desirability
4.89	1.50	0.969

### 3.2.2. Optimization

Numerical optimization was used to determine the optimum process parameters. In this study, the optimum values for the two factors of pH and mass of adsorbent were then identified by considering the highest removal for calcium, manganese and copper. Table 5 shows the optimum conditions for the maximum removal of calcium, manganese and copper. In the optimization process, copper was chosen due to its highest removal percentage among the three types of heavy metals used in the study. Table 6 shows the results for the removal of copper using model-predicted optimum values. Based on the results, the error and the standard deviation between the experimental value and the model response were 1.21 and 0.86, respectively. It showed that the removal percentage for copper predicted by the model were in good

agreement with the actual values using the above optimum conditions.

### 3.3. Adsorption isotherm study

Similarly to the optimization process, copper was selected in the isotherm study to study how copper ions interact with the PCFF adsorbent. Figs. 8 and 9, respectively illustrates the plot of Langmuir and Freundlich isotherms for copper removal.

#### 3.3.1. Langmuir isotherm

A graph of  $C_e/q_e$  vs.  $C_e$  is plotted in Fig. 8, where  $C_e$  is the concentration of heavy metal after the treatment (mg/L) and  $q_e$  is the amount of metal adsorbed per unit mass of adsorbent (mg/g). In Fig. 8, a line of best fit was drawn along the points with slope of  $1/Q_0$  and intercept of  $1/Q_0 b$ . The linear equation and  $R^2$  value could be obtained directly from the graph. The Langmuir constants related to maximum adsorption capacity ( $Q_0$ ) and rate of adsorption ( $b$ ) were calculated by using the simple mathematical calculation. The results of

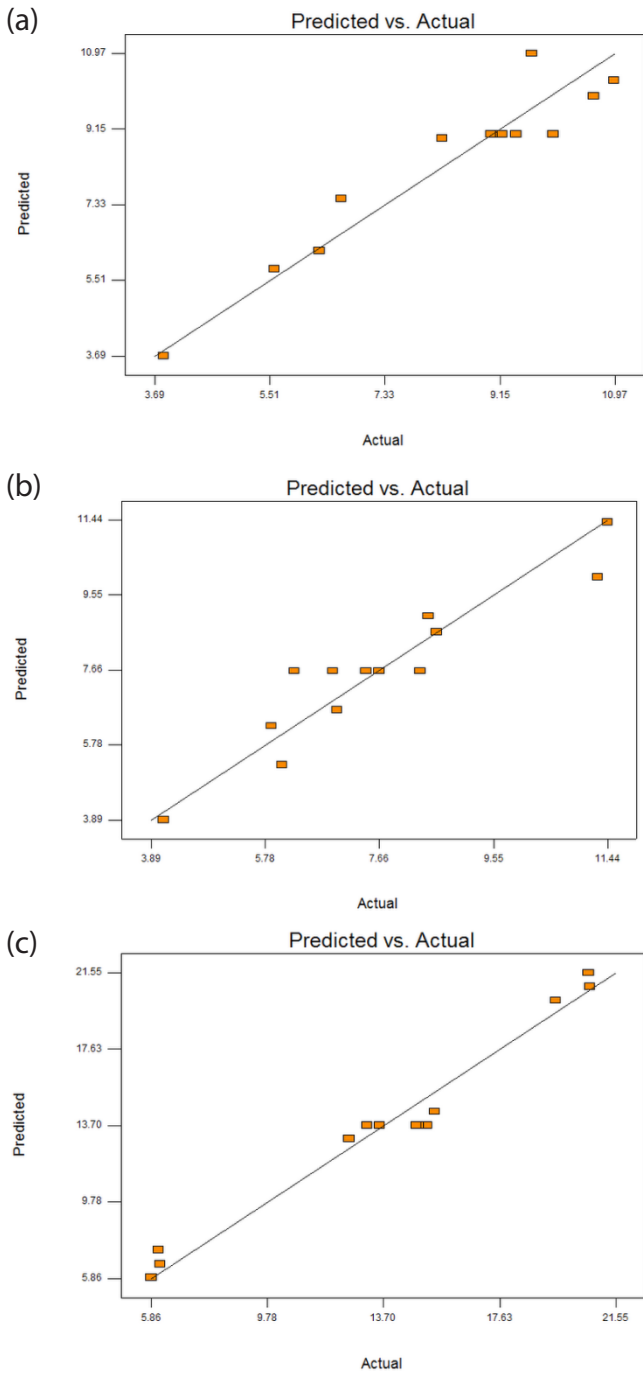


Fig. 6. Plots of predicted vs. actual values for (a) calcium, (b) manganese and (c) copper.

the Langmuir constants are summarized in Table 7. From the value of  $Q_o$ , it showed that the maximum adsorption capacity was only 2.0829 mg/g, with the adsorption rate constant of 0.0116 L/mg. This low adsorption capacity could be explained by the melting of keratin during the fast heating rate, as mentioned previously. The equilibrium parameter ( $R_L$ ) was calculated from Eq. (3). In this study, the  $R_L$  values computed (0.633–0.896) were in the range between 0 and 1 which indicated that the adsorption was favorable in the study.

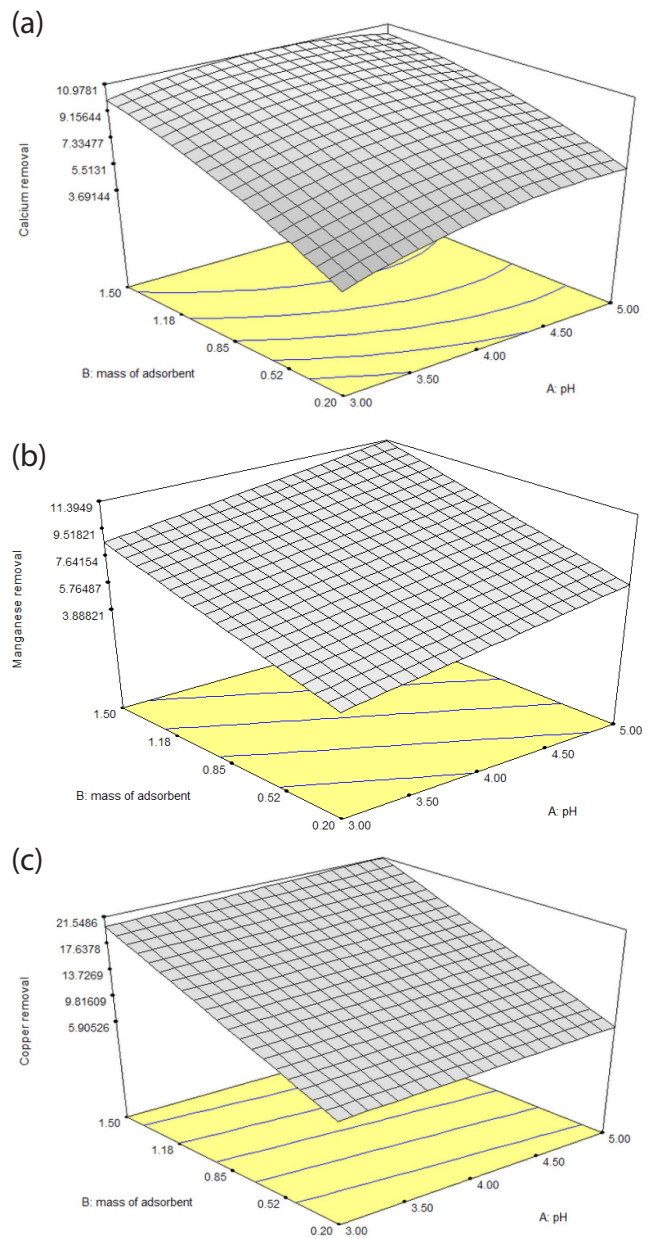


Fig. 7. 3D surface response for (a) calcium, (b) manganese and (c) copper.

Table 6  
Removal of copper using model-predicted optimum values

Experimental value	20.26%
Model response	21.47%
Error	1.21
Standard deviation	0.86

$$R_L = \frac{1}{1 + bC_o} \quad (3)$$

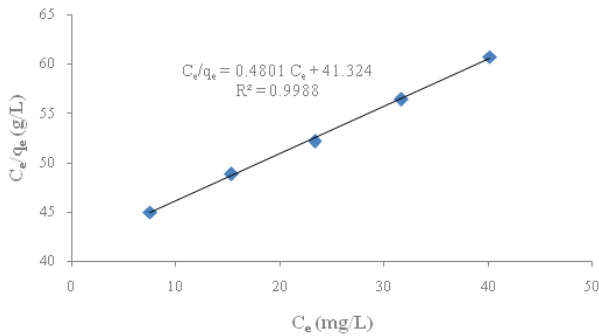


Fig. 8. Langmuir isotherm model for copper removal.

Table 7  
Results of the Langmuir constants

$Q_o$ (mg/g)	2.0829
$b$ (L/mg)	0.0116
$R^2$	0.9988

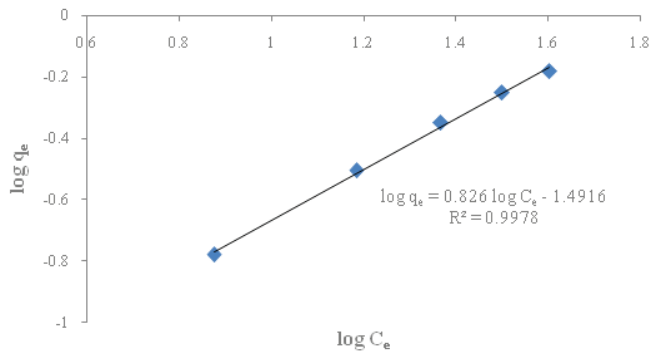


Fig. 9. Freundlich isotherm model for copper removal.

Table 8  
Results of the Freundlich constants

$K_F$ (mg/g)	0.0322
$1/n$	0.826
$N$	1.21
$R^2$	0.9978

### 3.3.2. Freundlich isotherm

In the Freundlich isotherm study, a graph of  $\log q_e$  vs.  $\log C_e$  was plotted with a line of best-fit yields a straight line with the slope of  $1/n$  and intercept of  $\log K_F$ . Fig. 9 illustrates the graph of Freundlich isotherm model. As shown in Fig. 9, the linear equation and  $R^2$  value could be obtained directly from the graph. Thus, the Freundlich constants of  $K_F$  and  $n$  could be calculated using the mathematical calculation. Table 8 summarizes the results of the Freundlich constants. The slope of  $1/n$  is a measure for the adsorption intensity or the surface heterogeneity, becoming more heterogeneous as

its value gets closer to zero [23]. In this study, the value of Freundlich intensity parameter ( $1/n$ ) was 0.826 which was below one, indicating a normal Freundlich isotherm. A relatively slight slope (with the  $n$  value of 1.21) as shown in the Freundlich plot (Fig. 9) indicated that the adsorption is good over the entire range of concentrations studied. From the value of capacity factor ( $K_F$ ), it showed that the quantity of adsorbate adsorbed for an equilibrium concentration was 0.0322 mg/g.

Based on  $R^2$  values shown the Tables 7 and 8, it can be deduced that the Langmuir equation yielded a better fit of the experimental data than the Freundlich equation as the value of  $R^2$  for Langmuir graph was closer to 1. Besides, the Langmuir constant of  $Q_o$  was more acceptable as compared to the Freundlich constant of  $K_F$  which was almost zero. Therefore, the adsorption isotherm for the copper removal was suitably described by Langmuir equation.

## 4. Conclusions

The performance of PCFF was investigated on the removal of heavy metals in this study. From the batch adsorption studies, copper obtained the highest removal, which was approximately 21% at pH 4 with 1.5 g of PCFF. As for calcium and manganese, the highest removals were around 11% at pH 5 with 1.5 g of PCFF, respectively. The experimental results showed that the adsorption ability of PCFF was low. However, previous studies focusing on the chemical treatment have been proved that CF has potential in removing heavy metals effectively. The poor adsorption exhibited by CF in this study may be due to the thermal treatment which causes the melting of keratin. Improvements in this phrase, focusing on the heating rate should be carried out. To date, less information has been reported in the thermal treatment on CF to remove heavy metals. Therefore, this study provides a useful baseline data on the characteristics of thermal treatment on CF for researchers to study the PCFF as a low-cost adsorbent.

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## Symbols

$b$	—	Empirical Langmuir constant related to rate of adsorption, L/mg
$C_e$	—	Final concentration of adsorbate, mg/L
$q_e$	—	Amount of adsorbate adsorbed per unit mass of adsorbent, mg/g
$K_F$	—	Empirical Freundlich constant or capacity factor, mg/g
$Q_o$	—	Empirical Langmuir constant related to maximum adsorption capacity, mg/g
$R_L$	—	Equilibrium parameter
$R^2$	—	Coefficient of determination
$1/n$	—	Freundlich intensity parameter



## References

- [1] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: a review, *J. Environ. Manage.*, 92 (2011) 407–418.
- [2] S. Martin, W. Griswold, Human health effects of heavy metals, *Environ. Sci. Technol.*, 15 (2009) 1–6.
- [3] A.R. Kumari, U.K. Babu, K. Sobha, Optimization of lead adsorption using animal biopolymers by factorial design, *Int. J. Sci. Innov. Discover*, 1 (2011) 303–319.
- [4] I.A. Aguayo-Villarreal, A. Bonilla-Petriciolet, V. Hernández-Montoya, M.A. Montes-Morán, H.E. Reynel-Avila, Batch and column studies of Zn<sup>2+</sup> removal from aqueous solution using chicken feathers as sorbents, *Chem. Eng. J.*, 167 (2011) 67–76.
- [5] I. Ali, M. Asim, T.A. Khan, Low cost adsorbents for the removal of organic pollutants from wastewater, *J. Environ. Manage.*, 113 (2012) 170–183.
- [6] X. Fan, Value-added Products from Chicken Feather Fiber and Protein, Ph.D. Thesis, Auburn University, Alabama, 2008.
- [7] A. Mittal, Adsorption kinetics of removal of a toxic dye, Malachite Green, from wastewater by using hen feathers, *J. Hazard. Mater.*, 133 (2006) 196–202.
- [8] H. Reynel-Avila, A. Bonilla-Petriciolet, G. De la Rosa, Removal of Cd (II) in Aqueous Solutions by Chicken Feathers, 8th World Congress of Chemical Engineering (WCCE8), Canada, 2009.
- [9] M.H. Jbara, Shrimp Pond Wastewater Treatment Using Pyrolyzed Chicken Feather (PCFF) As Adsorbent, M.Sc. Thesis, Universiti Sains Malaysia, Penang, 2013.
- [10] E. Senoz, R.P. Wool, Microporous carbon–nitrogen fibers from keratin fibers by pyrolysis, *J. Appl. Polym. Sci.*, 118 (2010) 1752–1765.
- [11] S. Al-Asheh, F. Banat, D. Al-Rousan, Beneficial reuse of chicken feathers in removal of heavy metals from wastewater, *J. Clean. Prod.*, 11 (2003) 321–326.
- [12] S. Sayed, S. Saleh, E. Hasan, Removal of some polluting metals from industrial water using chicken feathers, *Desalination*, 181 (2005) 243–255.
- [13] G. de la Rosa, H.E. Reynel-Avila, A. Bonilla-Petriciolet, I. Cano-Rodriguez, C. Velasco-Santos, A.L. Martínez-Hernández, Recycling poultry feathers for Pb removal from wastewater: kinetic and equilibrium studies, *Int. J. Chem. Biomol. Eng.*, 1 (2008) 394–402.
- [14] A. Mittal, Use of hen feathers as potential adsorbent for the removal of a hazardous dye, Brilliant Blue FCF, from wastewater, *J. Hazard. Mater.*, 128 (2006) 233–239.
- [15] A. Mittal, L. Kurup, J. Mittal, Freundlich and Langmuir adsorption isotherms and kinetics for the removal of Tartrazine from aqueous solutions using hen feathers, *J. Hazard. Mater.*, 146 (2007) 243–248.
- [16] A. Mittal, J. Mittal, L. Kurup, Utilization of hen feathers for the adsorption of indigo carmine from simulated effluents, *J. Environ. Prot. Sci.*, 1 (2007) 92–100.
- [17] E. Cervantes-González, L. Rojas-Avelizapa, R. Cruz-Camarillo, N. Rojas-Avelizapa, Feather waste as petroleum sorbent: a study of its structural biodegradation, *Proc. Annu. Int. Conf. Soils Sediments Water Energy*, 13 (2008) 50–58.
- [18] E. Senoz, Pyrolyzed Feather Fibers for Adsorbent and High Temperature Applications, Ph.D. Thesis, University of Delaware, Delaware, 2011.
- [19] E. Senoz, R.P. Wool, Hydrogen storage on pyrolyzed chicken feather fibers, *Int. J. Hydrogen Energy*, 36 (2011) 7122–7127.
- [20] G. Gassner III, W. Schmidt, M.J. Line, C. Thomas, R.M. Waters, Washing feathers, removal of solvent and removal of fibers, Google Patents, U.S., 1998.
- [21] E. Senoz, R.P. Wool, C.W. McChalicher, C.K. Hong, Physical and chemical changes in feather keratin during pyrolysis, *Polym. Degrad. Stab.*, 97 (2012) 297–307.
- [22] S.J. Hawkes, All positive ions give acid solutions in water, *J. Chem. Educ.*, 73 (1996) 516–517.
- [23] M.A. Muherei, R. Junin, Equilibrium adsorption isotherms of anionic, nonionic surfactants and their mixtures to shale and sandstone, *Mod. Appl. Sci.*, 3 (2009) 158–176.