Optimization of copper adsorption from synthetic wastewater by oil palm-based adsorbent using Central Composite Design

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Abstract. Oil palm empty fruit bunch (EFB) was chemically activated by phosphoric acid and heat treatment to produce porous activated carbon (AC) for adsorption of copper ions from synthetic wastewater using static batch test. Copper adsorption process was optimized using Response Surface Method (RSM) by varying four operating parameters i.e. pH (A), initial concentration (B), adsorbent dosage (C) and contact time (D) through a quadratic model developed based on Central Composite Design (CCD) approach. Within the tested parameter range, copper adsorption was found to be at optimum condition at pH 5, initial concentration of 200 mg/L, adsorbent dosage of 0.55 g per 200 mL copper solution and contact time of 2.5 hours, yielding 52.5% of copper removal. A good agreement was achieved by comparing the predicted model with experimental data ($R^2=0.9618$). All four operating parameters tested are significant in affecting the adsorption process, with pH being the most significant with an F-value of 171.70. The interaction between pH and initial concentration (AB) has the most significant interacting effects (F-value of 18.30), while quadratic effects of pH ($A^2$) and adsorbent dosage ($C^2$) are most significant with F-values of 62.80 and 42.58 respectively.

1. Introduction
Chemical intensive industries are among the most important industrial sectors throughout the world which directly boost job creation and the world’s economy. However, wastewater produced by chemical industries such as electroplating, fertilizer manufacturing, paper manufacturing, mining operations, tanneries, etc. contains heavy metals which inadvertently cause an adverse effect to the environment. Heavy metals are non-biodegradable, toxic, and carcinogenic and can easily accumulate in the living organisms, inducing serious health disorders if exposure exceeded permitted concentration [1]. Copper (Cu) is an example of common heavy metals found in industrial wastewater. Although copper is an important trace element in human bodies, excessive ingestion by an individual may cause liver damage, Wilson disease and insomnia [2]. Maximum acceptable concentration of divalent copper, Cu (II) in drinking water by World Health Organization (WHO) and Malaysian Ministry of Health are 2.0 mg/L and 1.0 mg/L respectively [3].

Among available methods for heavy metal removal from industrial wastewater, adsorption is highly recognized as viable option due to its efficiency, simplicity in design, economic feasibility and reversibility making adsorbent regeneration and copper recovery possible [4]. Natural adsorbents
made from agricultural wastes, typically called biosorbents, have received increasing attention due to their lower cost, better performance and higher availability [5]. At present, Malaysia and Indonesia occupy 85% of the palm oil production in the world which consequently increase the generation of palm oil wastes in the countries [6]. Therefore, many studies have employed oil palm wastes as adsorbents for removal of heavy metals such as manganese [7], cadmium [8], mercury, lead and copper [9], chromium [10] etc. Oil palm empty fruit bunches (EFB) can be a good precursor material for production of activated carbon due to its high carbon composition [11].

Previous work [9] showed that NaOH activated EFB was capable to remove several heavy metals including copper but copper removal efficiency was relatively low and the operating parameters had not been optimized by means of statistical analysis. Phosphoric acid (H₃PO₄) was found to develop activated carbon with high surface area and micropore volume [11], therefore, this work aims to investigate adsorption of copper from synthetic wastewater using chemically modified oil palm fibre waste and optimise the operating parameters using Central Composite Design (CCD). CCD is one of the effective response surface methods used to avoid unnecessary experiments, while at the same time considers possible synergy between the operating factors. The method has been employed by various studies to optimise adsorption of heavy metals [12-13]. Generally three operations i.e. 2n of factorial runs, 2n of axial runs and n₀ centre runs are characterized in CCD study [14].

2. Materials and methods

2.1. Material Preparation

Oil palm empty fruit bunch (EFB) fibre gathered from United Oil Palm Mill Sdn. Bhd., Nibong Tebal, Pulau Pinang was activated with phosphoric acid (85 vol. %) and heat treatment based on the method used by Ahmad et al. [15]. The EFB fibre was impregnated with H₃PO₄ solution at 1:1 (wt./vol.) ratio for 30 minutes and carbonised at 400°C in the furnace for 4 hours. The heated EFB was left to cool, washed with copious quantity of distilled water and then dried at 120°C for 24 hours in the oven. A stock solution of 1000 mg/L copper was prepared by dissolving analytical grade copper (II) nitrate (Cu(NO₃)₂) with deionised water. Dilution of stock solution was carried out using deionised water to prepare various initial concentrations of working solution.

2.2. Batch adsorption studies

The batch tests were carried out in 250 mL conical flasks, each filled with 200 mL of working solution and agitated at 135 rpm using an orbital shaker at room temperature. The operating parameters studied include pH (2-8), quite high initial concentration range (200-500 mg/L), low adsorbent dosage (0.1-1.0 g) and long contact time (1-4 hours) to observe which parameters and their interactions can further enhance copper removal. The copper concentration in the filtrate was analysed by colorimetric method using Hach 2800 Spectrophotometer. Copper removal percentage and adsorption capacity were calculated by Equations (1) and (2):

\[
\text{% Removal} = \frac{C_0 - C_e}{C_0} \times 100
\]

\[
Q_e = \frac{(C_0 - C_e)V}{M}
\]

Where \( C_0 \) and \( C_e \) represent the initial and final concentration (mg/L) respectively, \( V \) is the volume of solution (mL) and \( M \) is the mass of adsorbent (g).

2.3. Experimental design and model development

Design Expert Software Version 7.1.5 was used to study the significance of operating parameters and their interactions. The independent variables affecting copper adsorption i.e. pH, initial concentration,
adsorbent dosage, contact time were investigated at five different levels shown in Table 1: minimum (-1); centre (0); maximum (1) and 2 axial points (-α, α), based on a preliminary study.

Table 1. Independent variables matrix and encoded levels used in CCD.

| Independent variables            | Code | Levels |
|----------------------------------|------|--------|
| pH                              | A    | -α, -1, 0, +1, +α |
| Initial concentration (mg/L)     | B    | 200, 275, 350, 425, 500 |
| Adsorbent dosage (g)             | C    | 0.1, 0.33, 0.55, 0.78, 1.0 |
| Contact time (hrs)               | D    | 1, 1.75, 2.5, 3.25, 4 |

Copper removal percentage i.e. the response variable obtained from the experimental runs conducted based on suggestion by CCD was used to develop an empirical and quadratic model which correlates the four independent factors with the response, via a second-degree polynomial equation (Equation 3) as shown below, where Y is the response variable, β is the regressors and ε is the statistical error term [16].

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 D + \beta_{12} AB + \beta_{13} AC + \beta_{14} AD + \beta_{23} BC + \beta_{24} BD + \beta_{34} CD + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{44} D^2 + \epsilon$$  \hspace{1cm} (3)

2.4. Statistical analysis using ANOVA
Analysis of Variance (ANOVA) was performed using the same software used for CCD simulation to investigate the significance of model developed and to study the interactions of the independent variables and the dependent variable. A significant F-value implies that systematic variation is not included in the hypothesized model. A 95% confidence level is required to consider a relationship between observed and calculated results as reliable within the experimental range [17].

3. Results and discussion
3.1. Model development using CCD
A complete design matrix with response values acquired from the 30 experimental runs proposed by CCD is shown in Table 2. The empirical model which demonstrated the relationship between the operating parameters and copper removal can be expressed by Equation 4 below.

$$Y = 41.00 + 5.92(A) - 2.61(B) + 1.63(C) + 1.47(D) - 2.36(A)(B) - 1.67(A)(C) - 0.73(A)(D) + 1.26(B)(C) + 0.003125(B)(D) - 1.13(C)(D) - 3.35(A)^2 + 0.90(B)^2 - 2.76(C)^2 + 0.073(D)^2$$  \hspace{1cm} (4)

Where A stands for pH, B for initial concentration, C adsorbent dosage and D contact time. The positive sign in front of the variable denotes synergistic effect term while negative sign in front of the variable denotes antagonistic effect [18].

Additionally, regression analysis was also conducted to determine the relationship between actual experimental data and predicted values for copper removal percentage by activated EFB (Figure 1). The plot indicated that predicted copper removal percentage is in good agreement with the actual experimental values, with R² value of 0.9618.
Table 2. Design matrix with response values from experimental work.

| Run | Factor A: pH | Factor B: Initial concentration (mg/L) | Factor C: Adsorbent dosage (g) | Factor D: Contact time (hrs) | Response: Cu (II) removal (%) |
|-----|-------------|----------------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 1   | 3.50        | 275.00                                 | 0.33                          | 1.75                          | 23.43                         |
| 2   | 6.50        | 275.00                                 | 0.33                          | 1.75                          | 45.15                         |
| 3   | 3.50        | 425.00                                 | 0.33                          | 1.75                          | 21.62                         |
| 4   | 6.50        | 425.00                                 | 0.33                          | 1.75                          | 32.21                         |
| 5   | 3.50        | 275.00                                 | 0.78                          | 1.75                          | 30.19                         |
| 6   | 6.50        | 275.00                                 | 0.78                          | 1.75                          | 44.16                         |
| 7   | 3.50        | 425.00                                 | 0.78                          | 1.75                          | 33.65                         |
| 8   | 6.50        | 425.00                                 | 0.78                          | 1.75                          | 38.34                         |
| 9   | 3.50        | 275.00                                 | 0.33                          | 3.25                          | 31.55                         |
| 10  | 6.50        | 275.00                                 | 0.33                          | 3.25                          | 47.89                         |
| 11  | 3.50        | 425.00                                 | 0.33                          | 3.25                          | 28.56                         |
| 12  | 6.50        | 425.00                                 | 0.33                          | 3.25                          | 38.43                         |
| 13  | 3.50        | 275.00                                 | 0.78                          | 3.25                          | 33.23                         |
| 14  | 6.50        | 275.00                                 | 0.78                          | 3.25                          | 45.21                         |
| 15  | 3.50        | 425.00                                 | 0.78                          | 3.25                          | 36.33                         |
| 16  | 6.50        | 425.00                                 | 0.78                          | 3.25                          | 37.50                         |
| 17  | 2.00        | 350.00                                 | 0.55                          | 2.50                          | 15.48                         |
| 18  | 8.00        | 350.00                                 | 0.55                          | 2.50                          | 41.35                         |
| 19  | 5.00        | 200.00                                 | 0.55                          | 2.50                          | 52.52                         |
| 20  | 5.00        | 500.00                                 | 0.55                          | 2.50                          | 38.33                         |
| 21  | 5.00        | 350.00                                 | 0.10                          | 2.50                          | 28.44                         |
| 22  | 5.00        | 350.00                                 | 1.00                          | 2.50                          | 33.12                         |
| 23  | 5.00        | 350.00                                 | 0.55                          | 1.00                          | 40.78                         |
| 24  | 5.00        | 350.00                                 | 0.55                          | 4.00                          | 43.42                         |
| 25  | 5.00        | 350.00                                 | 0.55                          | 2.50                          | 41.56                         |
| 26  | 5.00        | 350.00                                 | 0.55                          | 2.50                          | 39.31                         |
| 27  | 5.00        | 350.00                                 | 0.55                          | 2.50                          | 38.36                         |
| 28  | 5.00        | 350.00                                 | 0.55                          | 2.50                          | 44.65                         |
| 29  | 5.00        | 350.00                                 | 0.55                          | 2.50                          | 38.33                         |
| 30  | 5.00        | 350.00                                 | 0.55                          | 2.50                          | 43.99                         |

Figure 1. Relationship between experimental and predicted values of copper removal.
3.2. Statistical significance of model

The model adequacy was further analysed using ANOVA and the results for the developed quadratic model are shown in Table 3. The model terms with Prob > F less than 0.05 can be considered significant [19-20]. In this case, the model is significant with an F-value of 27.00 and Prob > F less than 0.0001. For individual effects, all four factors studied, i.e. A (pH), B (initial concentration), C (adsorbent dosage) and D (contact time) are significant in the order of A > B > C > D.

| Table 3. ANOVA results for copper adsorption by chemically modified oil palm fibre. |
|---------------------------------------------------------------|
| Sum of square | df | Mean square | F-value | Prob > F |
| Model | 1851.60 | 14 | 132.26 | 27.00 | <0.0001 |
| A (pH) | 841.00 | 1 | 841.00 | 171.70 | <0.0001 |
| B (initial concentration) | 163.02 | 1 | 163.02 | 33.28 | <0.0001 |
| C (adsorbent dosage) | 63.80 | 1 | 63.80 | 13.03 | 0.0026 |
| D (contact time) | 51.71 | 1 | 51.71 | 10.56 | 0.0054 |
| AB | 88.78 | 1 | 88.78 | 18.13 | 0.0007 |
| AC | 44.59 | 1 | 44.59 | 9.10 | 0.0087 |
| AD | 8.42 | 1 | 8.42 | 1.72 | 0.2094 |
| BC | 25.58 | 1 | 25.58 | 5.22 | 0.0373 |
| BD | 1.562×10^{-4} | 1 | 1.562×10^{-4} | 3.190×10^{-5} | 0.9956 |
| CD | 20.45 | 1 | 20.45 | 4.18 | 0.0590 |
| A^2 | 307.57 | 1 | 307.57 | 62.80 | <0.0001 |
| B^2 | 22.41 | 1 | 22.41 | 4.57 | 0.0493 |
| C^2 | 208.55 | 1 | 208.55 | 42.58 | <0.0001 |
| D^2 | 0.14 | 1 | 0.14 | 0.030 | 0.8659 |
| Residual | 73.47 | 15 | 4.90 | - | - |
| Lack of Fit | 37.19 | 10 | 3.72 | 0.51 | 0.8277 |
| Pure Error | 36.28 | 5 | 7.26 | - | - |

For interacting effects, the significant model terms are AB (pH-initial concentration interaction), AC (pH-adsorbent dosage concentration) and BC (initial concentration-adsorbent dosage interaction). Meanwhile, for the quadratic effects, A^2 (pH), B^2 (initial concentration) and C^2 (adsorbent dosage) are the significant model terms. Among these factors, pH (as individual factor) is the most significant, with highest F-value of 171.70. In addition, the non-significance effect of ‘Lack of Fit’ test (P-value > 0.05) shows that the developed quadratic model fits well with the data.

3.3. Response surface estimation for optimum removal of copper

In this section, the influence of three significant interacting effects among the tested factors (AB, AC, and BC) on copper removal by modified oil palm fibre is discussed.

3.3.1. pH and initial concentration (AB). As can be seen in Figure 2, increasing pH value from 2 to 8 has led to a significant increase in copper removal when the initial copper concentration is low (200 mg/L). However, increasing the initial concentration from 200 to 500 mg/L has little influence on copper removal. A simultaneous increase in pH from 2 to 5 while increasing initial copper concentration contributes more significantly to copper removal. Further increase in pH values while increasing initial copper concentration however reduces the amount of copper ions removed. Similarly, a previous work using activated carbon produced from grape bagasse [21] also reported an optimum copper removal at around pH 5, while further pH increments also decreased the copper removal. It should be noted that at higher pH values, copper ions in the sample may be present in the
form of copper hydroxide (Cu(OH)$_2$) and thus can be removed from the solution by mechanism of precipitation instead of adsorption process [22-23]. Meanwhile at low pH level, the competitive adsorption that occurs between H$^+$ and Cu$^{2+}$ on the adsorbent surface may also contribute to lower percentage of copper removal [22-24].

Figure 2. Interacting effects of pH and initial copper concentration on copper removal.

3.3.2. pH and adsorbent dosage (AC). The interacting effects between pH and adsorbent dosage can be clearly observed in Figure 3. Increasing pH and adsorbent dosage both contribute to enhance copper removal up to an optimum at pH 5 and adsorbent dosage of 0.55 g. The efficiency of copper removal slightly deteriorates when tested beyond the optimal point of pH possibly due to the reasons discussed earlier. On the other hand, having more adsorbent dosage is also detrimental to copper removal attributed to the overlapping of active sites due to saturation of adsorbent particle and shielding effect on the outer layer, preventing the adsorbate to access the binding sites [25].

Figure 3. Interacting effects of pH and adsorbent dosage on copper removal.
3.3.3. Initial concentration and adsorbent dosage (AD). Figure 4 shows that copper removal increases when the adsorbent dosage is raised from 0.10 to the optimum dosage of 0.55 g at all initial copper concentrations as the availability of active sites for adsorbate binding is significantly increased. As discussed in the previous section, further increase in adsorbent dosage to 1.00 g adversely affects copper removal due to overcrowding and inaccessibility of sites. Meanwhile, low copper removal seen at higher initial copper concentration can be explained by saturation of the limited active sites, which blocks the adsorption sites preventing further adsorption to take place [26-27].

![Figure 4. Interacting effects between initial concentration and adsorbent dosage on copper removal.](image)

4. Conclusion
Optimisation of copper removal from synthetic wastewater using chemically modified oil palm-based adsorbent (EFB) was conducted by developing a quadratic model using Central Composite Design of response surface method. Four operating parameters were investigated i.e. pH, initial copper concentration, adsorbent dosage and contact time. Based on ANOVA, all four individual factors are observed to be statistically significant effect terms (within the range tested). Optimum condition for copper removal was found to be at pH 5, initial copper concentration of 200 mg/L, adsorbent dosage of 0.55 g and contact time of 2.5 hours. Among all factors tested, pH can be considered to play the most significant role in copper removal based on its highest F-value of 171.70. All interacting effects (pH-initial concentration, pH-adsorbent dosage and initial concentration-adsorbent dosage) are also statistically significant, whereby the synergy between pH and initial copper concentration is most favourable for copper removal. In addition, all quadratic factors show significant effects on copper removal except for contact time.

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