

Application of Response Surface Methodology (RSM) for Optimizing Production Condition for Removal of Pb (II) and Cu (II) Onto Kenaf Fiber Based Activated Carbon

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Abstract: This research aims to find out the feasibility of preparing kenaf fiber based carbon for removal of divalent cations of Pb (II) and Cu (II) from waste water. Activated carbon was prepared by using physiochemical activation method which involves two step of potassium hydroxide impregnation (KOH) with carbon dioxide activation of the semi carbonized char. The effects of three preparation variables; temperature (500-700°C), time (1-3 h) and Impregnation Ratio (IR) by using KOH (1-3) on the removal percentage of Pb (II) and Cu (II) ions were investigated by using Design of Experiment (DOE). Quadratic models were developed to correlate activated carbon preparation variables from kenaf fibers with the two responses by applying Central Composite Design (CCD). Experimental data were analysed by using analysis of variance (ANOVA) and the most influential factor on each experimental design response was identified. Process optimization was done by validating both the model to obtain maximum removal efficiency with possible maximum yield of activated carbon.

Key words: Activated carbon, ANOVA, Central Composite Design (CCD), Design of Experiment (DOE), Response Surface Methodology (RSM)

INTRODUCTION

Heavy metals can be defined as a group of transition and post transition metals in the periodic table and there are about 20 heavy metals identified which are extensively disseminated in ground and surface water. These heavy metals are highly toxic and persistent in nature and do not undergo any types of physical, chemical or microbial degradation. They can reach until the top member of food chain and have strong tendency to accumulate in living organisms. Thus they are imposing severe impact on human health and on the sustainability of ecosystem (Bailey *et al.*, 1999; Volesky, 2001; Cay *et al.*, 2004). As a result, there is an emergent concern about wide spread contamination of aqueous effluents by heavy metals for the last few decades. However, extensive research has been carried out to develop novel and potential adsorbent for elimination of toxic heavy metals from waste water. Adsorption onto commercial activated carbon is a well established and effective technique but its high costs have restricted its' widespread use.

In recent years, attempts have been taken to produce activated carbon from agro-based waste residues. The adsorption property of activated carbon is greatly prejudiced by its production conditions. The preparation variables of activating agent, temperature, time and impregnation ratio will persuade its surface area, pore size distribution and surface functional groups. Therefore, it is a challenge to produce explicit types of activated carbon which are suitable for definite applications. Many agricultural by-products such as coconut shell (Hu and Srinivasan, 1999), coffee bean husk (Baquero *et al.*, 2003), oil palm fiber (Hameed *et al.*, 2008), rubber wood sawdust (Srinivasakannan and Bakar, 2004), chestnut woods (Gomez-Serrano *et al.*, 2005), fruit stone (Puziy *et al.*, 2005), bamboo waste (Ahmad and Hameed, 2010), grain sorghum (Diao *et al.*, 2002), rattan sawdust (Ahmad *et al.*, 2009), cassava peel (Sudaryanto *et al.*, 2006), olive seed waste (Stavropoulos and Zabaniotou, 2005) have been successfully used to produce activated carbon due to their high carbon and low ash content.

The focus of this research was to explore the feasibility of producing activated carbon from kenaf by using Response Surface Methodology (RSM). The removal efficiency of Pb (II) and Cu (II) along with maximum possible yield can be increased by optimizing the operating factors. RSM has been used to determine the influences of individual preparation variables and their interactive influences. The RSM is a statistical technique for designing experiments, building models, evaluating the effects of several factors and searching optimum factors for desirable responses. By using this technique, the interactions of possible influencing parameters on treatment efficiency can be evaluated and optimized with a limited number of planned experiments (Lee *et al.*, 2000; Montgomery, 1997). RSM has been previously used for preparing activated carbon from olive waste cakes by physical activation (Stavropoulos and Zabaniotou, 2005), sewage sludge by chemical activation (Tay *et al.*, 2001), Turkish lignite by chemical activation (Karacan *et al.*, 2007), coconut shell (Gratiso *et al.*, 2008) and hazel nut shell (Sayan, 2006). The literature reflects that, no studies have been carried out on kenaf fiber based activated carbon to remove Pb (II) and Cu (II) ions from wastewater. A Central Composite Design (CCD) was selected to study simultaneously the effects of three factors: temperature, activation time and impregnation ratio on the two responses of percentage removal of Pb (II) and Cu (II) from waste water.

MATERIALS AND METHODS

Sample collection and adsorbent preparation: Kenaf fibers; collected from MARDI (Malaysian Agricultural Research and Development Institute) was washed with hot distilled water; it was dried at 105° for 24 h to remove all moisture. The dried samples were cut into small pieces of about 1-2 mm. Char was produced by semi carbonizing 40 g of dried fibers at 400°C for 2 h in inert atmosphere of nitrogen gas flow at 150 cm³/min in a tubular reactor. The char thus obtained was cool down at room temperature under nitrogen flow and stored in air-tight containers for further activation step. According to impregnation ratio, a precise amount of KOH pellets were mixed with 40 g of char and 250 mL deionized water. The mixture was occasionally stirred to dissolve the KOH pellets and consequently help them to penetrate inside the cellulose structure of the fibers. It was kept inside an oven over night at temperature 105°C for removal of water content and leaving only KOH onto the sample. The impregnation ratio can be calculated by using Eq. (1):

$$\text{Impregnation ratio (IR)} = \frac{W_{\text{KOH}}}{W_{\text{Char}}} \quad (1)$$

where, W_{KOH} = The dry weight of potassium hydroxide pellets and W_{char} = The dry weight of char.

Accurately weighted amount of KOH impregnated chars were placed inside the tubular furnace with nitrogen gas flow under the same condition mentioned above. The temperature was increased from room temperature to desired activation temperature. After reaching the desired activation temperature, the gas flow was changed to carbon dioxide at the same flow rate and kept constant for certain duration of time depending on the specific types of adsorbate (Pb or Cu) under consideration. Thus produced activated carbon was cooled to room temperature under nitrogen gas flow and the final product was washed with hot deionized water and few drops of 0.1 M hydrochloric acid (HCl) until the pH of the washing solution reached to 6-7. The washed samples was dried at 105°C in an oven until it was completely dried and stored in air-tight container for further applications.

Application of Design of Experiments (DOE): In this study, kenaf fiber based activated carbon was prepared by using two steps method of physiochemical activation. The preparation variables studied were x_i , activation temperature, x_{ii} , activation time and x_{iii} , impregnation ratio.

According to the software, Central Composite Design (CCD) was used to study the effects of the variables towards the responses of percentage removal of both the adsorbate of Pb (II) and Cu (II). This method is appropriate for fitting a quadratic surface and it is used to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters. In order to determine the relationship between the preparation variables and the responses under consideration, the data collected must be analyzed by a statistical approach of using regression equations (Montgomery, 1997). For regression equation, the preparation variables were coded according to Eq. (2):

$$x_i = \frac{X_i - X_i^x}{\Delta X_i} \quad (2)$$

where,

x_i = The coded value of the *i*th independent variable

X_i = The natural value of the *i*th independent variable

X_i^x = The natural value of the *i*th independent variable at the centre point

ΔX_i = The value of step change

According to central composite design, for each variable, a 2³ full factorial CCD for the three variables consisting of eight factorial points, six axial points and six replicates at the centre points were employed. However, for that altogether 20 experiments were necessary, and it can be calculated from Eq. (3).

Table 1: Independent variables and their coded levels for the central composite design

| Variables | Code | Units | Coded variable levels | | | | |
|--------------------|----------------|-------|-----------------------|-----|-----|-----|--------|
| | | | -α | -1 | 0 | +1 | +α |
| Temperature | X ₁ | °C | 431.82 | 500 | 600 | 700 | 768.18 |
| Activation time | X ₂ | h | 0.32 | 1 | 2 | 3 | 3.68 |
| Impregnation ratio | X ₃ | - | 0.32 | 1 | 2 | 3 | 3.68 |

Table 2: Experimental factors in coded and actual units and experimental responses

| Run | Type | X ₁ :Temp. | X ₂ :Time | X ₃ : IR | Temperature (°C) | Time (h) | IR | Cu removal (%) | Pb removal(%) | Yield |
|-----|--------|-----------------------|----------------------|---------------------|------------------|----------|------|----------------|---------------|-------|
| 1 | Center | 0 | 0 | 0 | 600 | 2 | 2 | 87.88 | 85.87 | 18.98 |
| 2 | Fact | -1 | 1 | 1 | 500 | 3 | 3 | 85.78 | 67.77 | 22.09 |
| 3 | Axial | 0 | -1.682 | 0 | 600 | 0.32 | 2 | 74.88 | 74.04 | 26.78 |
| 4 | Center | 0 | 0 | 0 | 600 | 2 | 2 | 86.90 | 86.54 | 17.78 |
| 5 | Fact | 1 | -1 | 1 | 700 | 3 | 1 | 94.99 | 86.89 | 14.99 |
| 6 | Center | 0 | 0 | 0 | 600 | 2 | 2 | 85.43 | 82.78 | 18.65 |
| 7 | Fact | 1 | -1 | -1 | 700 | 1 | 1 | 81.99 | 87.98 | 23.98 |
| 8 | Center | 0 | 0 | 0 | 600 | 2 | 2 | 88.45 | 85.45 | 17.99 |
| 9 | Axial | 0 | 0 | 1.682 | 600 | 2 | 3.68 | 95.77 | 78.99 | 13.99 |
| 10 | Fact | 1 | 1 | 1 | 700 | 3 | 3 | 93.99 | 93.98 | 5.77 |
| 11 | Fact | -1 | 1 | 1 | 500 | 3 | 1 | 80.99 | 64.99 | 32.09 |
| 12 | Fact | -1 | -1 | -1 | 500 | 1 | 1 | 78.99 | 63.98 | 33.89 |
| 13 | Fact | 1 | -1 | 1 | 700 | 1 | 3 | 82.22 | 89.99 | 19.99 |
| 14 | Fact | -1 | -1 | 1 | 500 | 1 | 3 | 86.88 | 66.09 | 26.99 |
| 15 | Center | 0 | 0 | 0 | 600 | 2 | 2 | 84.99 | 84.34 | 19.88 |
| 16 | Axial | 0 | 1.682 | 0 | 600 | 3.68 | 2 | 86.78 | 72.09 | 14.88 |
| 17 | Axial | 1.682 | 0 | 0 | 768.18 | 2 | 2 | 91.65 | 94.56 | 9.98 |
| 18 | Center | 0 | 0 | 0 | 600 | 2 | 2 | 87.99 | 83.99 | 16.67 |
| 19 | Axial | -1.682 | 0 | 0 | 431.82 | 2 | 2 | 75.87 | 65.09 | 34.99 |
| 20 | Axial | 0 | 0 | - | 600 | 2 | 0.32 | 80.43 | 71.09 | 27.89 |

$$N = 2^n + 2n + nc = 2^3 + 2 \times 3 + 6 = 20 \tag{3}$$

where, N = The total number of experiments required and n = The number of variables or factors.

The order of the experiments was randomized to diminish the effects of uncontrolled factors. Replicates at the central points were used to assess the residual error. The independent variables are coded to the (-1, 1) interval. The low and high levels are denoted by -1 and +1, respectively. The axial points are located at (0, 0, ±α), (0, ±α, 0) and (±α, 0, 0). Here, α is the distance of the axial point from center. Table 1 depicts the ranges and the levels of the preparation conditions studied here for this research.

The empirical model was developed for each response which correlated the response with three preparation variables by applying a second degree polynomial equation (Parajo *et al.*, 1992 and Azargohar and Dalai, 2005). This can be represented by following Eq. (4):

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \left(\sum_{i=1}^n b_{ii} x_i \right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j \tag{4}$$

where,

Y = The predicted response

b₀ = The constant coefficient

b_i = The linear coefficients

b_{ij} = The interaction coefficients

b_{ii} = The quadratic coefficients respectively

x_i and x_j = The coded values of the activated carbon preparation variables

Statistical analysis and model development: The regression parameters of the developed model and graphical interpretation for each response with statistical significance were calculated by using Design-Expert software (version 6, Stat-Ease, Inc., Minneapolis, USA). The relationship between the experimental variables and responses were evaluated by generating response surface and contour plots. The optimum values of the process variables for preparation of activated carbon for both types of adsorbate were determined by the software by means of numerical optimization from the menu. In that case, the goals for the variables of temperature, activation time and impregnation ratio were set within the studied range, where as removal percentage of both the cations along with yield was selected maximum. For process optimization, maximum product yield as well as adsorption performance were given emphasis to minimize the production cost which is extensively needed for commercialization of the prepared activated carbon.

Preparation of adsorbate: Lead (II) nitrate, copper (II) sulphate, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck, Germany. Stock solution of both the cations having concentration of about 1000 mg/L was prepared with double distilled

water. 100 mg/L test solution of Pb (II) and Cu (II) were prepared by successive dilution of the stock solution. The initial pH was adjusted to 5.5 using a pH meter (Mettles Toledo, Model: Ross FE 20, USA) so as to ensure true adsorption rather than precipitation. Dilution of the stock solution was done prior to each sorption study to reduce the error.

Adsorption studies: The batch experiment was carried out by adding 0.2 g of activated carbon with 50 mL of 100 mg/L solution of Pb (II) and Cu (II) and shaking at agitation speed of about 150 rpm until the equilibrium contact time. The remaining concentration of the cations was analyzed after predetermined intermission of time until the system reached equilibrium by using atomic absorption spectrophotometer (PerkinElmer Model 3100). The removal efficiency of the metal ion (Chowdhury *et al.*, 2011a, b) was calculated by using Eq. (5):

$$\text{Removal (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (5)$$

where,

C_i = Initial cation concentration (mg/L)

C_e = Equilibrium cation concentration (mg/L)

Surface characterization: Surface area, pore volume and pore diameter of the prepared adsorbent was measured by Autosorb1, Quantachrome Autosorb Automated gas sorption system supplied by Quantachrome. Before performing the nitrogen gas adsorption, the prepared activated carbon was outgassed under vacuum at temperature 300°C for 4 h to remove any moisture content from the solid surface. Surface area and pore volume were calculated by Brunauer Emmett Teller (BET). Above mentioned procedure was automatically performed by software (Micropore version 2.26) available with the instrument. The average bulk density was determined by water displacement of a definite amount of activated carbon.

Iodine number is one of the most fundamental parameter to characterize activated carbon. 0.1 g of activated carbon is mixed with 25 mL of iodine solution and was shaken for 1 min. After that the solution was filtered and 10 mL of filtrate was put inside a conical flask. The solution is titrated with 0.04 N sodium thio-sulphate solutions until it becomes clear. The iodine number for both the activated carbon was determined by using Eq. (6) which represents the number of milligrams of iodine adsorbed by one gram of activated carbon.

$$\text{Iodine Number} = V \times (T_i - T_f) \times C_i \times M_i / (T_i g) \quad (6)$$

where,

V = Volume of iodine solution 25 mL

T_i = Volume of Na_2SO_4 solution used for titration of 10 mL iodine solution

T_f = Volume of Na_2SO_4 solution used for titration of 10 mL of filtrate

G = Weight of activated carbon = 0.1 g

M_i = Molar weight of Iodine = 126.9044 g/mol

C_i = 0.045 N = Concentration of Iodine Solution

RESULTS AND DISCUSSION

Model development: The complete design matrix for 20 experimental run, including the coded and actual factors of variables together with the results obtained for removal percentage of both the cation is listed in Table 2.

The quadratic model was selected by the software for both the responses. Multiple regression analysis was used to correlate the responses of removal percentage with the three variables studied using a second order polynomial as shown above by Eq. (4). The quadratic regression models for removal percentage of Pb (II) ions, (Y_1) and removal percentage of Cu (II) ions, (Y_2) can be represented by following equations of (7) and (8):

$$Y_1 = 84.76 + 10.66X_1 + 0.17X_2 + 2.00X_3 - 1.29X_1^2 - 3.68X_2^2 - 3.68X_3^2 + 0.027X_1X_2 + 0.53X_1X_3 + 0.72X_2X_3 \quad (7)$$

$$Y_2 = 86.89 + 3.45X_1 + 3.35X_2 + 2.76X_3 - 0.77X_1^2 - 1.81X_2^2 + 0.76X_3^2 + 2.98X_1X_2 - 1.68X_1X_3 - 0.54X_2X_3 \quad (8)$$

Here, in Eq. (7) and (8), X_1 , X_2 , and X_3 represents the coded values for temperature, time and impregnation ratio. Positive sign in front of these three terms represents synergistic effect, while negative sign represents antagonistic effect. The coefficients with one factor of temperature, time and impregnation ratio represent the effect of that particular factor for the preparation of activated carbon. The coefficients with two factors and others with second order terms show the interaction between the two factors and quadratic effect, respectively.

The accuracy of the model developed can be understood by the value of R^2 , adjusted R^2 and standard deviation. R^2 indicates the ratio between sum of the squares (SSR) with total sum of the square (SST) and it describes up to what extent perfectly the model estimated experimental data points. Based on R^2 , it was observed that the experimental data fitted better for Pb (II) than Cu (II) onto the prepared activated carbon. Determination of CV value is essential as it indicates the ratio between standard error of estimate with the mean value of the observed response as percentage. It measures the reproducibility of the model. If the value

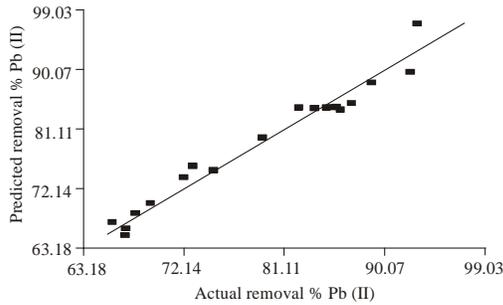


Fig. 1: Actual vs. predicted removal % of Pb (II) from waste water at pH 5.5

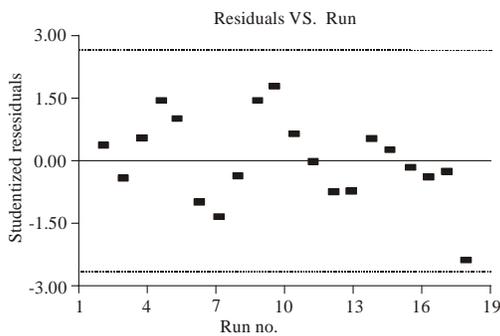


Fig. 2: Studentized residuals vs. experimental run number removal % of Pb (II) from waste water at pH 5.5

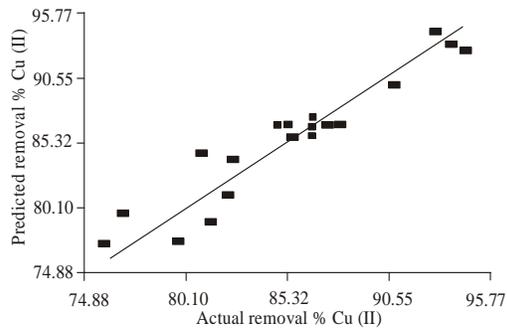


Fig. 3: Actual vs predicted Removal % of Cu (II) from waste water at pH 5.5

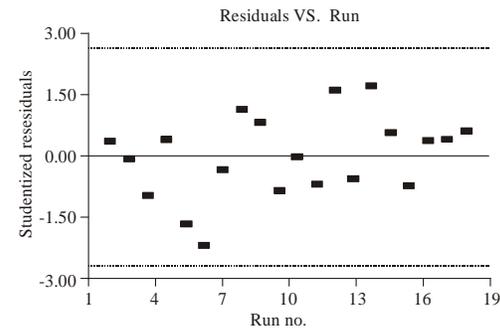


Fig. 4: Studentized residuals vs. experimental run number Removal % of Cu (II) from waste water at pH 5.5

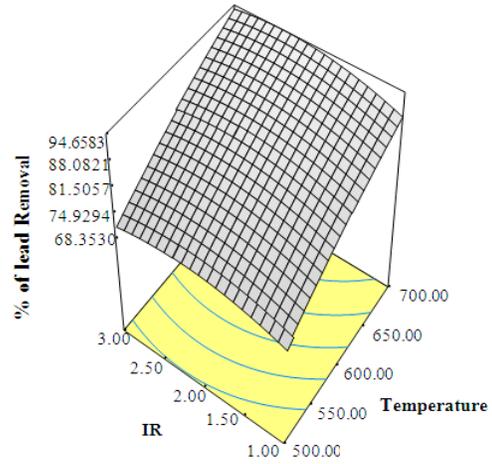


Fig. 5: The combined effect of temperature and Impregnation Ratio (IR) on the removal Percentage of Pb (II) from waste water

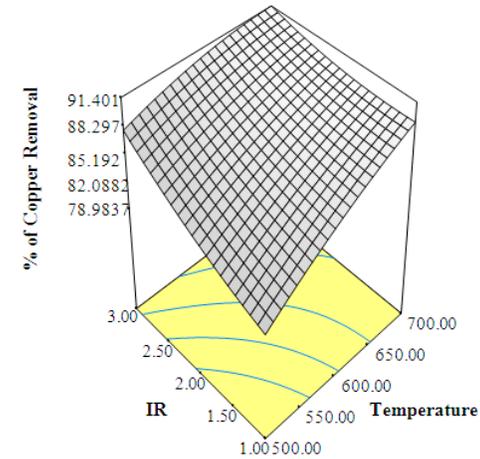


Fig. 6: The combined effect of temperature and Impregnation Ratio (IR) on the removal percentage of Cu (II) from waste water

Table 3: Statistical parameters obtained from the analysis of variances (ANOVA) for the models for Pb (II) and Cu (II) removal % from waste water

| Variable | Removal of Pb(II), Y_1 (%) | Removal of Cu(II), Y_2 (%) |
|------------------------------|------------------------------|------------------------------|
| Standard deviation, S.D. | 2.64 | 2.57 |
| Mean | 79.33 | 85.64 |
| Coefficient of variation, CV | 3.33 | 3.00 |
| R- squared (R^2) | 0.9648 | 0.8979 |
| R^2 adjusted | 0.9331 | 0.8061 |
| Adeq. precision | 19.184 | 10.575 |

is less than 10% then the model can be considered reasonably reproducible. It was found that the CV values obtained for percentage removal of Pb (II) and Cu (II) ions were 3.33 and 3.00 showing reproducibility of the

Table 4: Analysis of variances (ANOVA) and lack-of- fit test for response surface quadratic model for removal % of Pb (II) from waste water

| Source of data | SS | df | MS | F-value | Prob> F | Comments |
|-------------------------------|---------|----|---------|---------|---------|-------------|
| Model | 1914.93 | 9 | 212.77 | 30.45 | <0.0001 | Significant |
| X ₁ | 1551.91 | 1 | 1551.91 | 222.13 | <0.0001 | |
| X ₂ | 0.39 | 1 | 0.39 | 0.056 | <0.8170 | |
| X ₃ | 54.52 | 1 | 54.52 | 7.80 | <0.0190 | |
| X ₁ ² | 23.98 | 1 | 23.98 | 3.43 | 0.0937 | |
| X ₂ ² | 195.15 | 1 | 195.15 | 27.93 | 0.0004 | |
| X ₃ ² | 128.12 | 1 | 128.12 | 18.34 | 0.0016 | |
| X ₁ X ₂ | 0.0061 | 1 | 0.0061 | 0.0009 | 0.9771 | |
| X ₂ X ₃ | 4.15 | 1 | 4.15 | 0.59 | 0.5849 | |
| X ₃ X ₁ | 2.23 | 1 | 2.23 | 0.32 | 0.4588 | |
| Residuals | 69.86 | 10 | 6.99 | | | |
| Pure Error | 9.54 | 5 | 1.91 | | | |

Table 5: Analysis of variances (ANOVA) and lack-of- fit test for response surface quadratic model for removal % of Cu (II) from waste water

| Source of data | SS | df | MS | F-value | Prob> F | Comments |
|-------------------------------|--------|----|----------|---------|---------|-------------|
| Model | 582.29 | 9 | 64.70 | 9.78 | 0.0007 | significant |
| X ₁ | 162.36 | 1 | 162.36 | 24.53 | 0.0006 | |
| X ₂ | 152.81 | 1 | 152.81 | 23.09 | 0.0007 | |
| X ₃ | 104.12 | 1 | 104.12 | 15.73 | 0.0027 | |
| X ₁ ² | 8.62 | 1 | 8.621.30 | 1.13 | 0.2804 | |
| X ₂ ² | 47.17 | 1 | 47.17 | 7.13 | 0.0235 | |
| X ₃ ² | 8.35 | 1 | 8.35 | 1.26 | 0.2876 | |
| X ₁ X ₂ | 71.22 | 1 | 71.22 | 10.76 | 0.0083 | |
| X ₂ X ₃ | 2.34 | 1 | 2.34 | 0.35 | 0.0943 | |
| X ₃ X ₁ | 22.61 | 1 | 22.61 | 3.42 | 0.5650 | |
| Residuals | 66.18 | 1 | 06.62 | | | |
| Pure error | 10.35 | 5 | 2.07 | | | |

Table 6: Process parameters optimization for Pb (II) and Cu (II) by design of experiment (DOE) from waste water

| Process parameter | Pb (II) Based activated carbon | Cu (II) based activated carbon | Predicted removal % of Pb (II) | Experimental removal % of Pb (II) | Predicted removal(II) % of Cu | Experimental removal(II) % of Cu |
|-------------------------|--------------------------------|--------------------------------|--------------------------------|-----------------------------------|-------------------------------|----------------------------------|
| Temperature | 700°C | 500°C | | | | |
| Time (h) | 1 | 1.25 | 87.82 | 93.23 | 86.98 | 96.54% |
| Impregnation Ratio (IR) | 1.35 | 3 | | | | |

Table 7: Surface characterization of prepared activated carbon

| Physio-chemical properties | Activated carbon Pb | Activated carbon Cu |
|--|--------------------------|--------------------------|
| P _{ZPC} | 6.99 | 6.58 |
| Iodine number | 510.67mg/g | 310.22 mg/g |
| BET surface area | 525.50 m ² /g | 330.40 m ² /g |
| Langmuir surface area | 624.40 m ² /g | 557.80 m ² /g |
| Micropore surface area (t-Method) | 151.9 m ² /g | 180.2 m ² /g |
| Total pore volume | 0.322 cm ³ /g | 0.189 cm ³ /g |
| Average pore diameter | 24.9 | 22.9 |
| Cumulative adsorption surface area (DH Method) | 516.6 m ² /g | 182.0 m ² /g |
| DR- method for micro-pore surface area | 610.2 m ² /g | 381.4 m ² /g |
| Bulk density | 0.353 g/mL | 0.332 g/mL |

models. The correlation coefficient R² and adjusted R², CV and standard deviation for both the cations is listed in Table 3.

The performance of the model can be observed by the plots of predicted versus experimental percentage removal by Fig. 1 and 3. In Fig. 2 and 4, the plot of studentized residuals versus run order was tested and the residuals were scattered randomly around ±3.00. This was an indication of better fit for both the models with the experimental data.

Statistical significance of the model: The competence and significance of the model was justified by analysis of variance (ANOVA). The ANOVA for the quadratic

model for removal percentage of Pb (II) is listed in Table 4. The model F-value observed was 30.45 enlightening that the model was significant. Values of Prob> F less than 0.05 reflects that the model terms were significant. Here, X₁, X₃, X₂² and X₃² were significant model terms.

Table 5 depicts the results of analysis of variance (ANOVA) for percentage removal of Cu (II). The F-value of 9.78 inferred that the model was significant. Value of Prob> F less than 0.05 also indicated that the model terms were significant. In this case, X₁, X₂, X₃, X₂² and interaction terms of X₁X₂ were significant model terms. Nevertheless, the statistical results calculated here showed that the above mentioned two models were

well defined to predict the removal percentage of both the cations within the range of variables applied here for preparation of activated carbon. In this research, for the percentage removal for Pb (II) and Cu (II), "Adeq. Precision" obtained were 19.184 and 10.575, respectively which measures the signal to noise ratio. The ratio determined were greater than 4, representing that model can be used to navigate the design space.

Effect of production condition on removal percentage (%): The 3D surface graphs and contour plots for removal percentage of both the cations are represented by Fig. 5 and 6. These figures demonstrate the effects of activation temperature and impregnation ratio on the responses of percentage removal of Pb (II) and Cu (II) from aqueous solution by keeping the time-2 hour constant.

The curvature observed in the Fig. 5 and 6 represents that, prominent effect of activation temperature and impregnation ratio on removal percentage. From the plot, it reveals that the temperature and impregnation ratio is proportional with the removal percentages. It seems that, up to a certain limit; the increase of temperature and impregnation ratio will enhance the reaction between KOH and char in presence of CO₂, resulting more porous structure suitable for adsorption. Significance test showed that activation time has got less impact on removal percentage. It was described by previous researchers also that, the activation time had least impact on the development of surface area and pore structure of the activated carbon prepared from cassava peel and the pore characteristics were subjective strongly by KOH impregnation ratio and temperature (Sudaryanto *et al.*, 2006). However, the three preparation variables studied here have positive effects on absorption capacity of Pb (II) and Cu (II) ions from waste water.

Optimization and verification of the model: For industrial based production of activated carbon, product yield is expected high to reduce operational cost. It was observed from the Table 2 that, maximum yield was achieved when all the variables were minimum and lowest yield was observed at highest temperature, impregnation ratio and time. On the other hand, maximum removal percentage of Pb (II) was observed at temperature 768.18°C, 2 h and impregnation ratio of 2. For Cu (II), comparatively lower temperature, time and impregnation ratio was sufficient to eliminate maximum percentage of copper reflecting its' higher affinity towards the prepared activated carbon. This phenomenon can be explained on the basis of different physio-chemical properties of both the cations. Copper has relatively small ionic radius of 0.73Å than lead having ionic radius of 1.19Å; which makes copper easier to diffuse into the layers of activated carbon. Moreover, according to Irving William series, copper

has got highest tendency to form stable complexes than lead. For this reason, it was observed that, in all 20 experimental run; copper was absorbed more than lead. At high temperature and impregnation ratio, the surface area and pore size of the prepared activated carbon was more to capture larger ions like lead but failed to retain smaller cations like copper. May be at higher temperature, some surface functional groups which can form complexes with copper was destroyed due to thermal degradation. Consequently, in equilibrium contact time, less amount of copper was adsorbed by the activated carbon. It was observed by previous researchers also that, for heavy metal adsorption, surface area is not only the main factor, pore size distribution and surface functional groups also play vital role to adsorbed metallic cations. To optimize maximum removal percentage for both the cations with highest yield under the same condition is difficult because the interest regions are quite different. Numerical optimization was done for both the cations separately by using the Design-Expert software. The goals for the preparation condition were targeted within the range and the removal percentage along with the yield was set maximum for successful commercialization of the product. Following Table 6 depicts optimum values for preparation condition of lead and copper based activated carbon along with yield by the software. From the condition given by the software, it was observed that comparatively less temperature and high ratio was selected by the software for adsorption of copper reflecting its greater affinity towards the prepared activated carbon. Model validation was done by preparing both types of activated carbon according to the condition given by the software and batch experiments were conducted to find out experimental percentage removal. It was found that the values given by the software was in accordance with the experimental values with relatively small error percentage.

Surface characterization of prepared activated carbon: Table 7 summarizes the properties of activated carbon prepared under optimum condition for both the adsorbate chosen by the software. It was again observed that activated carbon prepared for Pb (II) had more surface area, pore diameter and iodine number than Cu (II) based activated carbon as higher temperature and impregnation ratio were employed to prepare the activated carbon.

CONCLUSION

From the findings of this research, it can be concluded that kenaf fiber can be converted successfully as an effective adsorbent by making activated carbon from it by physiochemical activation method. The activated carbon thus prepared can remove divalent cations of Pb (II) and Cu (II) quite efficiently from

waste water. In that case, commercial production of activated carbon from kenaf fiber can be easily utilized to treat Pb (II) and Cu (II) rich industrial effluents.

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