

# Adsorption Studies of Heavy Metals on Coal Fly Ash Samples from Aqueous Solutions

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Received December 05, 2021; Revised January 11, 2022; Accepted January 20, 2022

**Abstract** The study focused on assessing the reduction of wastewater toxicity due to heavy metals after treating with fly ash. Fly ash can be a byproduct usually considered as waste material in coal-based thermal power plants. Since Fly ash has the potential to adsorb heavy metal ions, it may be considered a byproduct of a thermal power plant and used as an effective adsorbent to treat industrial wastewater. The present study examined the adsorption capacity of fly ash to adsorb Cd, Cu, and Pb from wastewater under different conditions of contact time, pH, and adsorbent dosages. The uptake of metal ions by fly ash generally rises with increasing pH. Compared to adsorptions at higher temperatures, heavy metal adsorptions were more pronounced at ambient temperatures. The removal % of Cu, Cd and Pb ions increases with increasing adsorbent dose from 4 to 16 g/L, further increase in adsorbent dosage has little effect. Significant reduction in Cd (79%), Cu (98%), and Pb (79%) contents after treatment with fly ash at an optimum flyash dose of 16 g/L. A regression equations for percent removal for Cu Cd and Pb metal ions were generated using Minitab software (trial vesion) and models were tested for their significance by ANOVA test. The isotherm models demonstrate that the heterogeneous nature of the adsorbent controls the adsorption of metals. The utility of flyash sample for removal of metal ion to treat regional metallurgical industrial/ textile effluent shows a sustainable route and best usage of thermal plant waste towards sustainable goal.

**Keywords:** fly ash, adsorption, wastewater, removal

**Cite This Article:** Ishwari B.K, Kumar P.S, and Shivaprasad K.H, “Adsorption Studies of Heavy Metals on Coal Fly Ash Samples from Aqueous Solutions.” *Applied Ecology and Environmental Sciences*, vol. 10, no. 1 (2022): 25-33. doi: 10.12691/aees-10-1-5.

## 1. Introduction

Industrialization has posed a tremendous environmental problem due to the release of heavy metals as waste into the environment. The present-day primary concern is that heavy metal ions do not degrade, and their presence creates toxicity to many life forms [1]. Aqueous wastes of industries, such as metallurgical plants, electroplating, foundry, alloy making industries, photo printing enterprises, increase heavy metal contamination [2]. Hence, the treatment of water to remove toxic heavy metals in industrial discharge is a worldwide concern. Precipitation followed by coagulation is a proven method for the removal of heavy metals from wastewater. Membrane filtration is another effective way of removing heavy metals due to its high capital cost, limiting its usage in industrial practice [3]. Among the effluents treatment methods, viz., ion exchange, adsorption, and co-precipitation/adsorption, adsorption is an effective technique for removing heavy metals from industrial wastewater. The activated carbon is a widely used adsorbent [3] and has shown good metal ion adsorption capacities [4-8] for treating industrial wastewater.

Recently activated carbon has found its usage in various applications, including cosmetics, has raised its demand, and has become expensive. In the quest for low cost, abundantly available adsorbents, many researchers have reported their studies on various adsorbents such as Rice husk [9,10,11,12,13], sugarcane bagasse [14,15,16,17,18], sawdust [19,20,21], coconut shell [22], palm shell [23], etc. for removal of heavy metals from industrial wastewater. However, the adsorbent cost information is seldom reported, and the expense of individual sorbents varies depending on the degree of processing if required and its local availability. In general, the adsorbent is low cost if it is abundant in nature or a byproduct or waste from any industry [34].

Hence, to explore all possible sources of low-cost adsorbents, their feasibility for removing heavy metals should be studied in detail. Bellary Thermal Power station (BTPS) is located in Kudatini Village, Bellary District, in the Indian state of Karnataka. Three coal-fired units generate 21 lakh MT of Fly ash (FA) per annum. The FA is identified as a cheap adsorbent for adsorption of organic substances, heavy metal ions, dyes in wastewater [24,25]. The advantage of fly ash is that it contains unburnt carbon. Therefore, the choice of using this fly ash as an adsorbent is obvious. This study aims to assess the BTPS Fly ash for

treating local metallurgical industrial effluents and thereby contribute to the search for less expensive adsorbents and their utilization possibilities for treating heavy metal ions in industrial wastewater.

## 2. Materials and Methods

### 2.1. Fly Ash as an Adsorbent

The coal fly ash (FA) was collected from the Ballari Thermal Power Station, Ballari, in Karnataka, India. The FA was oven-dried at 70°C, sieved to a particle size of 100 µm, and stored in a polythene bag. The specific surface area was measured using the BET (Brunauer-Emmett-Teller) method, and the loss on ignition was calculated by heating the pre-heated sample [35]. The mineralogy of the ash was determined by employing Rigaku mini flex X-ray diffractometer (XRD) with CuK $\alpha$  radiation. The surface morphology of fly ash was observed under a Scanning electron microscope (JEOL

JSM-5800). The adsorption of heavy metal ions by low-cost adsorbents was evaluated under various conditions such as adsorbent quantity, pH, heavy metal concentration, and contact time through kinetic and isotherm studies.

Figure 1 shows the particle size analysis of collected coal fly ash (FA) from the Ballari Thermal Power Station, Ballari, in Karnataka, India. It is evident from the graph that the fly ash sample contains nearly 80% >53 µ. The specific surface area was found to be 32 m<sup>2</sup>/gm. The fly ash used in this study shows the loss on ignition of 7%, which is marginally higher than the upper limitation of 6% as stipulated by ASTM C618. Figure 2, the X-ray diffractogram of fly ash, shows SiO<sub>2</sub> as a primary mineral and Al<sub>2</sub>O<sub>3</sub>, Mullite, and Biotite as minor minerals. Figure 3 shows the scanning electron microscope image and Energy Dispersive Spectra (EDS) of the fly ash sample. The surface morphology of the ash particles shows that they are irregular in their shape, and the majority of the particles are solid. Some particles are spherical in shape and hollow. Occasionally, cenosphere particles are also observed.

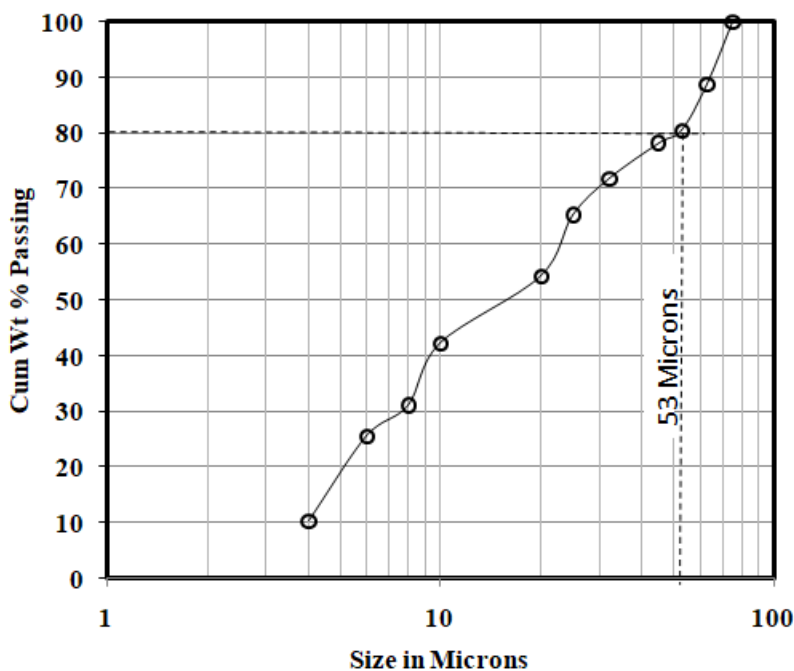


Figure 1. Particle Size analysis of Fly Ash

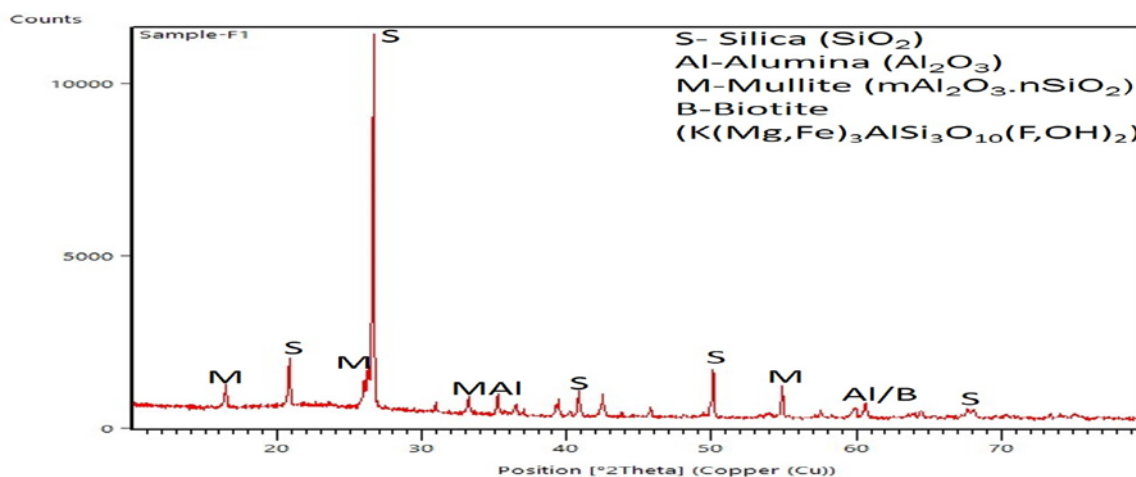


Figure 2. X-Ray Diffraction of Fly Ash Sample

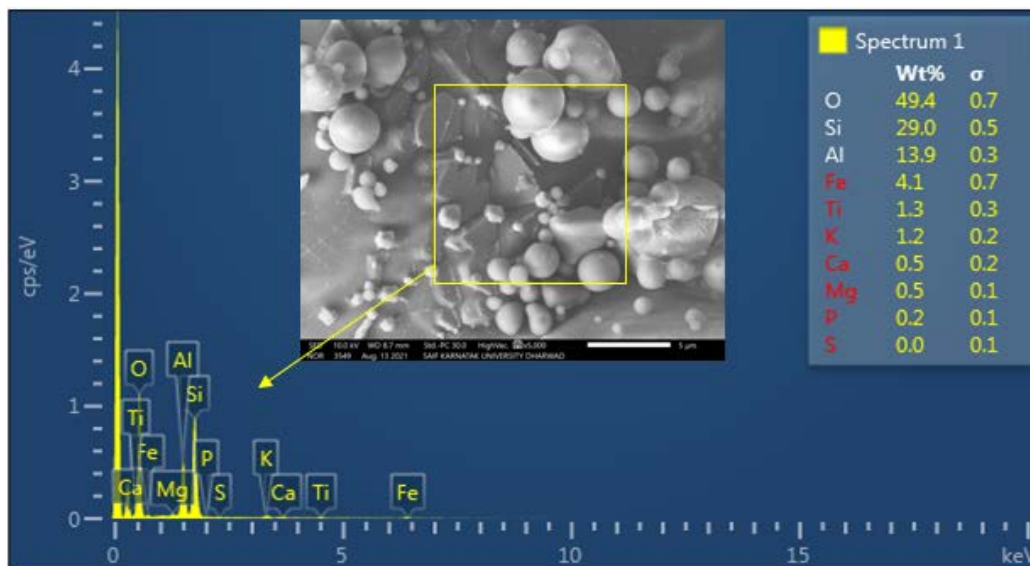


Figure 3. Scanning Electron Microscopy of Fly Ash Sample

## 2.2. Preparation of Stock Solution of Heavy Metals

All chemicals used in this study are of analytical grade and procured from Ranbaxy India Limited. Distilled water was used for all purposes unless expressly stated.

The stock solutions of 100 mg/L were prepared by dissolving 0.163g of  $\text{CdCl}_2$ , 0.393g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and 0.160g of  $\text{Pb}(\text{NO}_3)_2$  in 1000 mL of demineralized water.

## 2.3. Initial Metal Concentration Studies

The stock solutions were diluted to desired concentrations (5, 10, and 20 mg/L), out of which 50mL were taken for each adsorption experiment. Batch adsorption studies were carried out for different initial metal concentrations. Accurately weighed adsorbent was added to 50 mL of heavy metal solutions taken in 100 mL stoppered bottles. After adjusting to the desired pH, they were stirred well on a magnetic stirrer for varying periods. After adsorption, the solutions were centrifuged, filtered and the clear solutions were analyzed for metal content using AAS.

## 2.4. Contact Time

50 mL of metal solution (5, 10, 20 mg/L) was taken in a 100 mL stoppered bottle and the solution was adjusted to pH 5, and 16g/L of fly ash was added to it. This adsorbent adsorbate slurry was stirred well and allowed to equilibrate for varying periods of 60, 90, 120, and 150 minutes time interval. After the stipulated period, the clear liquid was analyzed for Cd, Cu, Pb concentrations with AAS (Varian AA-975 and AA-1275 model). Experiments were carried out simultaneously for other periods.

## 2.5. Adsorption Studies

Adsorption studies using fly ash as an adsorbent for removing metal ions are complex because fly ash is a basic material. When fly ash placed in an aqueous system, the surface becomes negatively charged and the pH of the study system shift towards higher pH conditions. Batch

adsorption experiments were carried out using a magnetic stirrer, a series of stoppered bottles containing predetermined amounts of fly ash and heavy metal ions at different pH levels. The slurry pH was adjusted in the range of 2-10 using dilute  $\text{HNO}_3/\text{NH}_3$  and stirred on a magnetic stirrer for 15 min until the pH was stabilized. Then the metal solutions were added to the bottles to make initial concentrations of 5-20 mg/L. The contents were further agitated for different periods and until the equilibrium was reached. The slurry was centrifuged and filtered using the Gooch crucible. The residual concentration of heavy metals was determined by using an atomic absorption spectrometer (AAS). The removal of metal ions was calculated using the following equation:

$$H = \frac{C_o - C_e}{C_e} \cdot 100 \quad (1)$$

H is the percent removal of metal ions (%), and  $C_o$  and  $C_e$  are the initial and equilibrium concentrations of metal ions in solution (mg/L).

## 2.6. pH Studies

The effect of pH on sorption was also studied by varying the pH of the slurry from 2-10. metal ion solutions obtained the Langmuir isotherms at different adsorbent doses (5-20) g/L at different times (60, 90, 120, and 150 min) metal concentration of 10 mg/L at room temperature.

## 2.7. Statsical Analysis

For adsorption process, it is important to know the influence of control factors upon the % emoval of the heavy metals from solutions. Factorial design is used to reduce the total number of experiments in order to achieve the best percentage removal (%Cd) of cadmium ions, (%Cu) of Copper ions, (%Pb) of Lead ions. The general full factorial design of experiments determines which factors have important effects on a response (% Removal) as well as interactional effects of factors at different levels. The number of experimental runs are shown in Table 1. In this study, The design was mean to investigate the effect

of Ph (5 levels; 2, 4, 6, 8, 10) and heavy metal concentration in solution (3 Levels; 5, 10 and 20 mg/l) as shown in Table 2. Total of 15 experiments were obtained by using statistical software package MINITAB 17. The response is the percentage removal of cadmium (%Cd), Copper (%Cu), Lead (%Pb). The prediction of output response (% Removal) is performed by fitting the experimental data to a regression model, as illustrated in Equation (1) below:

$$\begin{aligned}
 & (\% \text{ Removal})_{(Cd, Pb, Cu)} \\
 & = b_0 + \sum_{i=1}^k b_i A_i + \sum_{j=1}^k b_j B_j + \sum_{i=1}^k \sum_{k=1}^k b_{ij} A_i B_j \quad (1)
 \end{aligned}$$

where,  $A_i$  and  $B_j$  are independent coded variables;  $i$  and  $j$  are respective level for each variable,  $b_0$  is a constant;  $b_i$  and  $b_j$  are regression coefficient for linear effects;  $b_{ij}$  is regression coefficient for interaction effect.

Table 1. Experimental runs for Full Factorial Design

| Run No | pH of Solution | Metal Conc (Mg/l) | % Removal |      |      |
|--------|----------------|-------------------|-----------|------|------|
|        |                |                   | Cu        | Cd   | Pb   |
| 1      | 6.0            | 20.0              | 78.5      | 43.4 | 64.2 |
| 2      | 8.0            | 20.0              | 98.2      | 54.8 | 78.1 |
| 3      | 10.0           | 5.0               | 93.7      | 77.3 | 71.5 |
| 4      | 8.0            | 5.0               | 92.3      | 63.4 | 66.4 |
| 5      | 2.0            | 5.0               | 28.3      | 7.8  | 4.5  |
| 6      | 4.0            | 20.0              | 64.6      | 26.5 | 3.1  |
| 7      | 2.0            | 20.0              | 39.6      | 15.2 | 7.5  |
| 8      | 2.0            | 10.0              | 32.4      | 12.6 | 6.2  |
| 9      | 6.0            | 5.0               | 71.3      | 48.9 | 39.8 |
| 10     | 6.0            | 10.0              | 74.8      | 57.8 | 53.9 |
| 11     | 10.0           | 20.0              | 98.6      | 68.5 | 79.6 |
| 12     | 10.0           | 10.0              | 98.4      | 79.5 | 76.2 |
| 13     | 4.0            | 5.0               | 63.5      | 19.8 | 18.3 |
| 14     | 4.0            | 10.0              | 63.2      | 24.8 | 22.7 |
| 15     | 8.0            | 10.0              | 97.8      | 66.4 | 74.5 |

Table 2. Factors and numbers of levels investigated in full factorial design

| Factors                    | Notation | Levels (in Coded) |    |    |     |     |
|----------------------------|----------|-------------------|----|----|-----|-----|
|                            |          | 1                 | 2  | 3  | 4   | 5   |
| pH of solution             | A        | 2                 | 4  | 6  | 8   | 10  |
| Metal Concentration (mg/l) | B        | 5                 | 10 | 20 | --- | --- |

The analysis of variance (ANOVA) method was chosen to evaluate the effect of operating factors to responses of a particular developed process. In this study, through ANOVA, the significant effects of pH of solution (A) and Heavy metal concentration (B) on the responses, such as % Removal of (Cd, Cu and Pb) could be determined, by observing 'probability-value' upon the analysis. Most researchers have mutually agreed that the p-value has to be equal or smaller than 0.05 so that the operating factors are statistically significant in affecting the investigated response.

## 3. Results and Discussion

### 3.1. Effect of Adsorbent Dosage

A initial set of experiments to quantify the optimum adsorbent dosage for effective removal of metal ions was conducted using fly ash samples with different doses varying from 4 to 20 g/L for 3 h at  $28 \pm 2^\circ\text{C}$ . Figure 4 shows that the percentage of metal adsorbed gradually increases as the adsorbent dosage increases from 4 to 16 g/L and remains almost constant after that. This is attributed to increased surface area or available adsorption sites with increased dosage (Ozacar and Sengil 2005). The decrease in effective surface area and the number of available sites, different adsorbent dosage in a fixed volume of adsorbate reduces percent adsorption (Namasivayam et al. 1998). It is also evident from Figure 4 that, above 16 g/L of adsorbent dosage, the increase in metal uptake becomes insignificant. Thus, optimum dose refers to the minimum adsorbent dose corresponding to the maximum removal. From Figure 4, the optimum dose of fly ash is 16 g/L. Adsorbent recorded a maximum metal removal capacity of 98, 79, and 79 % for Cu, Cd, and Pb, respectively, at optimum dosage (16 g/L) and 120 min contact time.

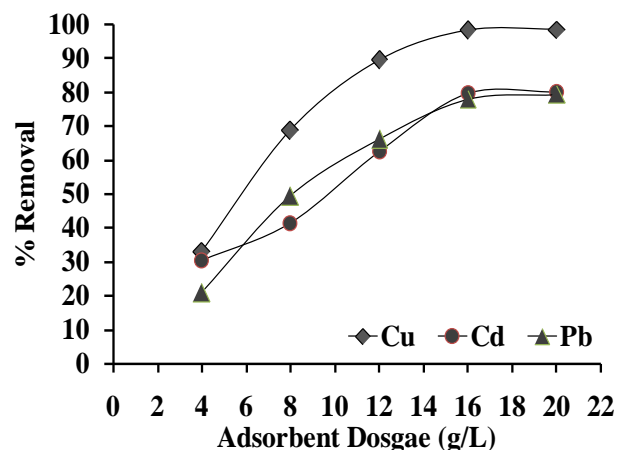


Figure 4. Effect of Adsorbent dosage on % Removal of metal ions

### 3.2. Effect of Contact Time

Contact time is one of the critical parameters in the adsorption process. Figure 5 depicts that the adsorption is heterogeneous with an initial rapid rate followed by slower rates. Maximum removal of metals happened within 120 min of agitation and subsequently remained almost constant. Thus, the adequate contact time or equilibrium time taken was 120 min. In 2 h (in about 120 min), 98 % of Cu, 80 % of Cd, and Pb were adsorbed. The rapid adsorption rates in the initial hours are likely due to free adsorption sites being more in the initial stage, and the slow absorption rate in the later stage is due to saturation of the active adsorbent sites [36]. Hence, the subsequent test were carried with a constant contact time of 120min.

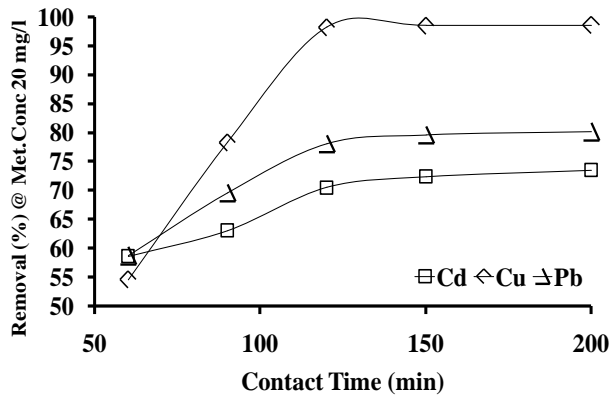


Figure 5. Effect of Contact time on % Removal

### 3.3. Regression Analysis

The regression analysis includes correlation of coefficient ( $R^2$ ), coefficient of each factor, values of constant, p-value and subsequently, regression equation. The experimental and predicted values of responses are tabulated in Table 3. The results showed that, the  $R^2$  values of regression equations for all the heavy metal (% removal) are significant Table 4. Meanwhile, the complete details of coefficient of each factor, values of constant and p-value are shown in subsequent section. The p-value would indicate the significance of this constant and regression coefficient in the developed regression model.

Table 3. Experimental and Predicted response

| Expt Run | % Removal(Cu) |           | % Removal(Cd) |           | % Removal(Pb) |           |
|----------|---------------|-----------|---------------|-----------|---------------|-----------|
|          | Actual        | Predicted | Actual        | Predicted | Actual        | Predicted |
| 1        | 78.5          | 77.75     | 43.4          | 47.27     | 64.2          | 52.63     |
| 2        | 98.2          | 98.99     | 54.8          | 58.77     | 78.1          | 73.00     |
| 3        | 93.7          | 93.71     | 77.3          | 74.09     | 71.5          | 75.77     |
| 4        | 92.3          | 92.91     | 63.4          | 60.53     | 66.4          | 73.00     |
| 5        | 28.3          | 30.24     | 7.8           | 10.86     | 4.5           | 6.07      |
| 6        | 64.6          | 66.65     | 26.5          | 20.93     | 3.1           | 14.70     |
| 7        | 39.6          | 36.32     | 15.2          | 9.10      | 7.5           | 6.07      |
| 8        | 32.4          | 33.74     | 12.6          | 15.64     | 6.2           | 6.07      |
| 9        | 71.3          | 71.67     | 48.9          | 49.03     | 39.8          | 52.63     |
| 10       | 74.8          | 75.17     | 57.8          | 53.81     | 53.9          | 52.63     |
| 11       | 98.6          | 99.79     | 68.5          | 72.33     | 79.6          | 75.77     |
| 12       | 98.4          | 97.21     | 79.5          | 78.87     | 76.2          | 75.77     |
| 13       | 63.5          | 60.57     | 19.8          | 22.69     | 18.3          | 14.70     |
| 14       | 63.2          | 64.07     | 24.8          | 27.47     | 22.7          | 14.70     |
| 15       | 97.8          | 96.41     | 66.4          | 65.31     | 74.5          | 73.00     |

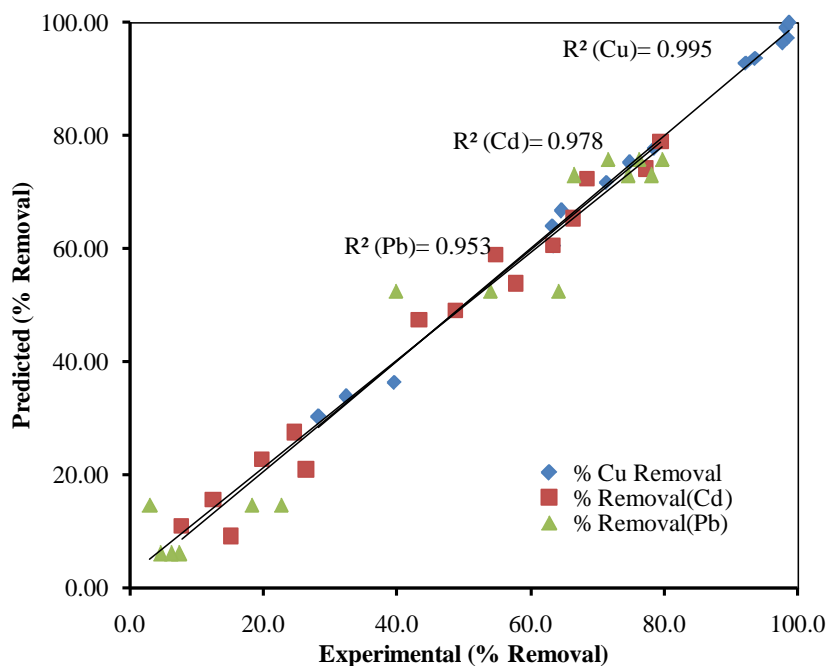


Figure 6. Relation between predicted and Experimental values of % Removal (Cu, Cd, Pb)



Table 4. Regression model analysis of % removal

| Responses    | R <sup>2</sup> | R <sup>2</sup> (Adjusted) | R <sup>2</sup> (Predicted) | Model   |
|--------------|----------------|---------------------------|----------------------------|---|
| % Cu Removal | 99.57%         | 99.24%                    | 98.48%                     | $73.01 - 39.58(A_1) - 9.247(A_2) + 1.853(A_3) + 23.09(A_4) + 23.89(A_5) - 3.193(B_1) + 0.3067(B_2) + 2.887(B_3) - 1.940(A_1B_1) - 1.340(A_1B_2) + 3.280(A_1B_3) + 2.927(A_2B_1) - 0.8733(A_2B_2) - 2.053(A_2B_3) - 0.3733(A_3B_1) - 0.3733(A_3B_2) + 0.7467(A_3B_3) - 0.6067(A_4B_1) + 1.393(A_4B_2) - 0.7867(A_4B_3) - 0.006667(A_5B_1) + 1.193(A_5B_2) - 1.187(A_5B_3)$ |
| % Cd Removal | 97.81%         | 93.46%                    | 89.48%                     | $44.45 - 32.58(A_1) - 20.75(A_2) + 5.587(A_3) + 17.09(A_4) + 30.65(A_5) - 1.007(B_1) + 3.773(B_2) - 2.767(B_3) - 3.060(A_1B_1) - 3.040(A_1B_2) + 6.100(A_1B_3) - 2.893(A_2B_1) - 2.673(A_2B_2) + 5.567(A_2B_3) - 0.1267(A_3B_1) + 3.993(A_3B_2) - 3.867(A_3B_3) + 2.873(A_4B_1) + 1.093(A_4B_2) - 3.967(A_4B_3) + 3.207(A_5B_1) + 0.6267(A_5B_2) - 3.833(A_5B_3)$         |
| % Pb Removal | 95.33%         | 93.46%                    | 89.48%                     | $44.43 - 38.37(A_1) - 29.73(A_2) + 8.200(A_3) + 28.57(A_4) + 31.33(A_5) - 4.333(B_1) + 2.267(B_2) + 2.067(B_3) + 2.767(A_1B_1) - 2.133(A_1B_2) - 0.6333(A_1B_3) + 7.933(A_2B_1) + 5.733(A_2B_2) - 13.67(A_2B_3) - 8.500(A_3B_1) - 1.000(A_3B_2) + 9.500(A_3B_3) - 2.267(A_4B_1) - 0.7667(A_4B_2) + 3.033(A_4B_3) + 0.06667(A_5B_1) - 1.833(A_5B_2) + 1.767(A_5B_3)$       |

Table 4 depict the regression analysis for % removal (Cd, Cu, Pb). p-Values for the constants were 0.000, indicating that the constants were significant in the regression models (Equations (2)-(4)). Figure 6 shows the relationship of predicted and the experimental data points indicating that all the % removal models (Eq 2-4) has made good agreement (R<sup>2</sup> of 0.995 and 0.978 and 0.953 for removal of Cu, Cd and Pb respectively). Any deviation from the operating range of the process variable such as beyond the higher/lower level would affect the adsorption performance.

### 3.2.1. Effect of pH and Metal Concentration on % Removal

The influence of pH on the adsorption of Cd, Cu, and Pb ions was investigated with a fixed amount of adsorbent, i.e., 16 g/L in the slurry. Batch experiments were carried out as per the design shown in Table 1 at different pH values (from 2 to 10) and different metal concentrations (5 to 20 mg/l) of the solution, and the results are depicted in Figure 7(a,b & c). pH played an essential role in determining the role of adsorption of various species. The surface chemistry of adsorbent and solution chemistry of metal ions change significantly when pH changes.

Contour plots are drawn to represent the regression model, showing prediction of responses (% Removal) according to desired factors (pH and Heavy Metal Concentration). The contour plots for percent removal of Cd, Cu and Pb are shown in Figure 6(a,b& c). Figure 7(a) shows the effect of solution pH and the Cd metal ion concentration on the removal %. The initial contours refers to percent removal of Cd<sup>2+</sup> ions has been found to decrease with increasing concentration. Initially, the lower adsorption capacity of Cd by the adsorbent is attributed to the higher H<sup>+</sup> concentration, which in turn interacts with

Cd for adsorption on the active sites of the adsorbent surface. At low solution pH, the adsorption of Cadmium must overcome the repulsive force between the positively charged particles. At pH values between 2.0 and 10.0, the major chemical states of Cadmium were Cd<sup>2+</sup> (minor) and Cd(OH)<sup>+</sup> (major). As the affinity of Cd(OH)<sup>+</sup> was better than that of Cd<sup>2+</sup> it can be adsorbed on the adsorbent surface not only by electrostatic adsorption and ion exchange but also by hydrogen bonds. With the further increase in the solution pH, the protonation sites on the adsorbent surface decreased, and the negative charge increased, facilitating the adsorption of Cd<sup>2+</sup> and Cd(OH)<sup>+</sup> on the deprotonation active sites of the adsorbent by electrostatic adsorption. Hence, the increase in pH is beneficial to the adsorption of heavy metal cadmium with 79 % removal of Cd in a solution having a Cd concentration of 10 mg/l.

Contour plot would be useful in evaluating the significant effects of the pH and variation in metal concentration in solution to the final adsorption of heavy metals. Figure 7b shows that the maximum percent removal of copper ions on the adsorbents was observed at pH values ranging from 6 to 10 and significantly decreased by reducing the pH values. A straight contours attributes that no change in removal % is observed when the metal concentration of the slurry in the range from 10 to 20 mg/l, a slight decrease of metal removal % is observed that might be explained by the fact that the adsorption sites are no more affected by the metal ion concentration change after reaching the saturation limit. In the pH range between 8 and 10, 98% removal of Cu ions was achieved.

Figure 7c shows the Pb adsorption was maximum at pH 8, and a sharp increase from 63 to 79% was observed (Figure 7c) between pH 6 and 8. It is observed that metal

concentration in the solution exceeds 10 mg/L, the metal uptake becomes less significant.

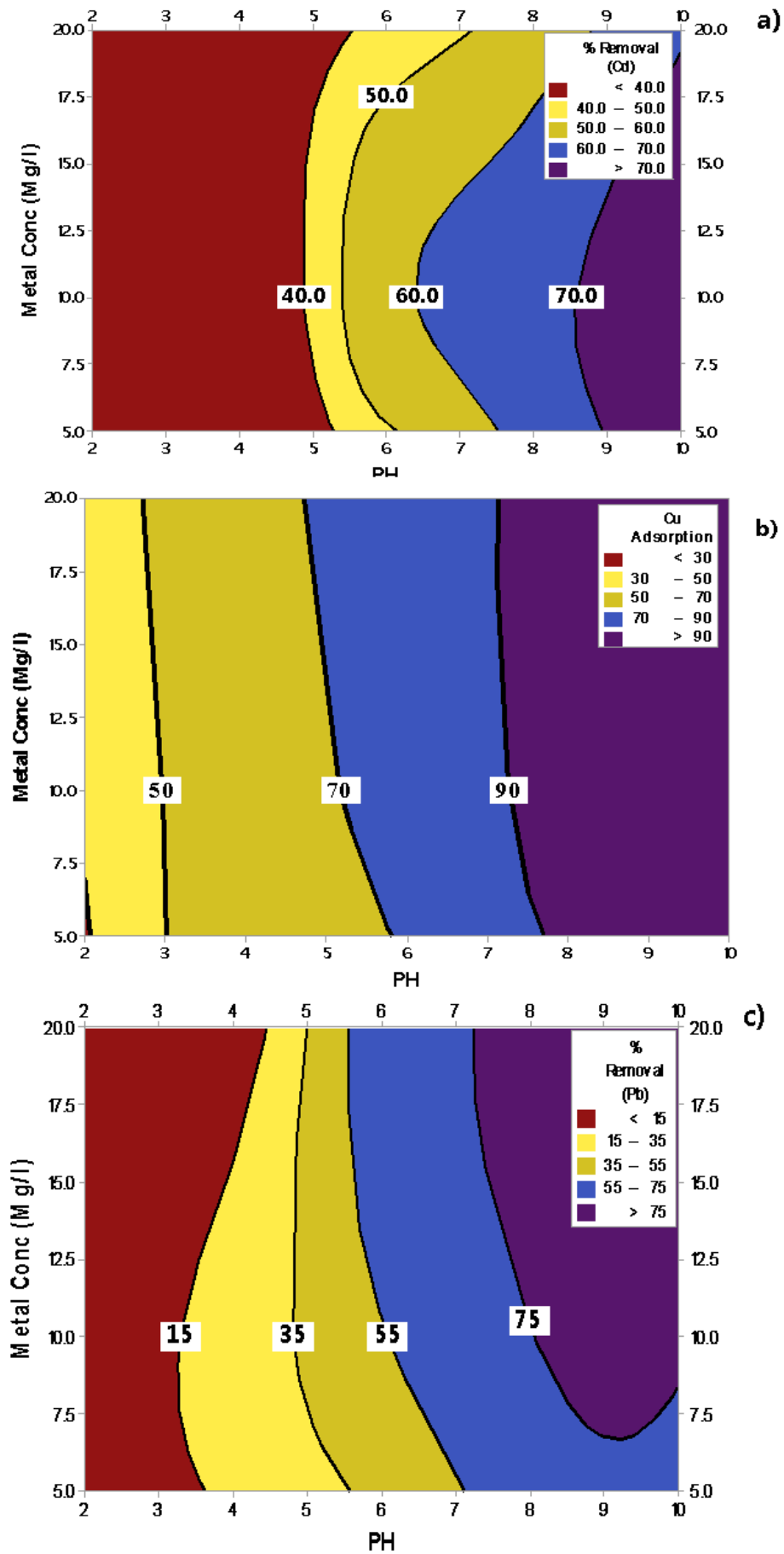


Figure 7. Effect of pH and Metal concentrations on a) % Cd Removal, b) % Cu Removal, c) % Pb Removal

### 3.2.2. Analysis of Variance (ANOVA)

The analysis of variance (ANOVA) method was conducted to evaluate significant effect of operating factors on the responses of a process [26,27,28,29]. In this case, through ANOVA, the significant effects of pH (A) and metal ion concentration in solution (B) on the responses, such as percent removal of heavy metals (Cd, Cu and Pb) could be determined, by observing probability value, or also commonly known as 'p-value' upon the analysis. It is found that the probability value (P-value) of the independent variables (pH and metal concentration) of the adsorption process conditions are less than 0.05 in linear relationships and in interaction the P value more than the significant value i.e 0.05 for all the three models. The model deficiencies were justified by the  $R^2$  values, the  $R^2$  values of the percent removal of Cd, Cu and Pb models and suggests that all the models was highly significant than and indicate that the regression line perfectly fits the data.

### 3.5. Adsorption Isotherms Models

In the present study, the Langmuir adsorption isotherms were used (Peric et al., 2004). Adsorption isotherms describe the surface properties of adsorbents. The plot of the isotherms is shown in Figure 8, and model parameters are tabulated in Table 5. The basic assumption of the Langmuir model is that the formation of a monolayer takes place on the surface of the adsorbent, and the intermolecular forces decrease with the distance. It is also assumed that the adsorbent surface is homogeneous and possesses similar and energetically equivalent adsorption sites [30-34].

It was presented as

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

A linear Langmuir adsorption isotherm is presented in Figure 8. The values of  $q_m$  and  $K_L$  of linear expression of Langmuir adsorption isotherm were calculated from the

slopes and intercept of the linear plot of  $C_e/q_e$  versus  $C_e$  in Figure 8 and Table 5.

$$\frac{1}{q_e} = \frac{1}{q_m} + \left( \frac{1}{K_L q_m} \right) \left( \frac{1}{C_e} \right) \quad (6)$$

The isotherm was found to be linear over the entire concentration range with an excellent linear correlation coefficient ( $R^2_{(Pb)} = 0.975$ ,  $R^2_{(Cu)} = 0.942$ ,  $R^2_{(Cd)} = 0.972$ ). Figure 8 shows that the Langmuir equation represents the best experimental data fit than any other isotherm equation. Since the Langmuir equation assumes that the surface is homogeneous, the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor ( $R_L$ , also called equilibrium parameter), which is defined by the following equation 7.

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (7)$$

$C_0$  (mg/L) is the initial dye concentration and  $K_L$  (L/mg) is the Langmuir constant related to adsorption energy. The value of  $R_L$  shows the shape of the isotherms to be either unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ). The influence of isotherm shape on whether adsorption is favorable or unfavorable has been considered. For a Langmuir type adsorption process, the isotherm shape can be classified by a dimensionless constant separation factor ( $R_L$ ), given by Eq. (4). It was observed that lower  $R_L$  values at higher initial  $C_R$  concentrations showed that adsorption was more favorable at higher concentrations. The degrees tended toward unity (the completely linear case).

Table 5. model details

| Heavy Metals | Langmuir     |              |       | $R_L$ |
|--------------|--------------|--------------|-------|-------|
|              | $Q_m$ (mg/g) | $K_L$ (L/mg) | $R^2$ |       |
| Cd           | 0.037        | 1.202        | 0.972 | 1.0   |
| Cu           | 0.262        | 0.046        | 0.942 | 1.0   |
| Pb           | -0.079       | 0.596        | 0.975 | 1.0   |

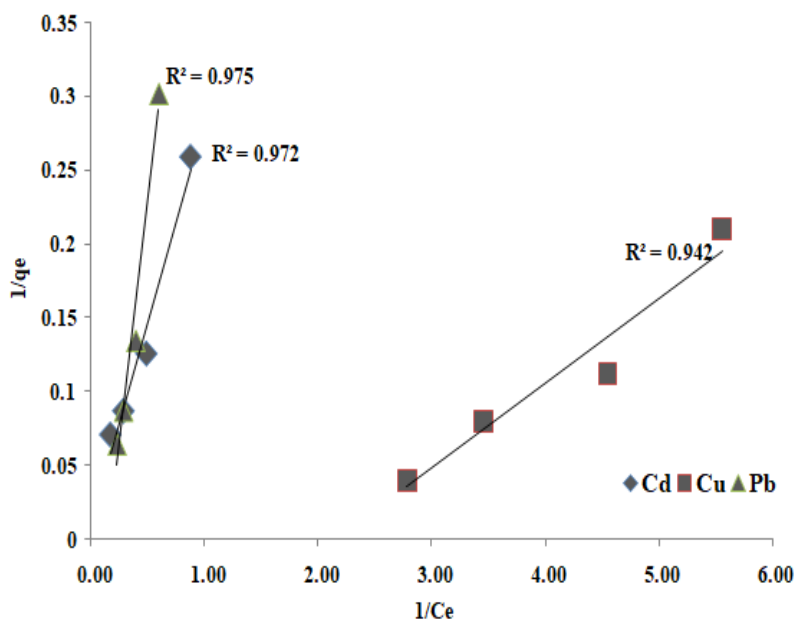


Figure 8. Langmuir isotherm model for various metals onto Flyash



## 4. Conclusions

The fly ash sample received from Ballary thermal power station, Ballary, Karnataka, India, is studied for its utility as an adsorbent for removing heavy metals (Cd, Cu and Pb) by adsorption. The fly ash consisted of SiO<sub>2</sub> as primary mineral and Al<sub>2</sub>O<sub>3</sub> and Mullite and Biotite as minor minerals. The adsorption rate of metals was found to attain equilibrium after 120 min. The removal % ions increase with increasing adsorbent dose from 4 to 16 g/L; an optimum dose of fly ash for metal removal was found to be 16 g/L with the removal efficiency of 98% of Cu, 78% of Cd and Pb, respectively. The isotherm models demonstrated that the heterogeneous nature of the adsorbent controls the adsorption of metals. The utility of flyash sample for removal of metal ion to treat regional metallurgical industrial/ textile effluent shows a sustainable route and best usage of thermal plant waste towards sustainable goal.

## Acknowledgements

The author IBK acknowledges KSUF, Karnataka University, Dharwad for extending their support in SEM and EDS analysis of the flyash sample.

## References

- [1] V.K. Gupta, M. Gupta, S. Sharma, Process development for removing lead and chromium from aqueous solution using red mud - an aluminum industry waste, *Water Res.* 35 (5) (2001). 1125-1134.
- [2] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Removal of heavy metal from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste, *Bioresour. Technol.* 76 (2001). 63-65.
- [3] S. Chand, V.K. Aggarwal, P. Kumar, Removal of hexavalent chromium from the wastewater by adsorption, *Indian J. Environ. Health* 36 (3) (1994). 151-158.
- [4] Gaikwad RW, *Electron J. Environ Agric Food Chem* 2004; 3(4): 702.
- [5] Pesavento M, Profumo A, Giancarla Alberti G, Fabio Conti F. *Anal Chim Acta* 2003; 480: 171.
- [6] Qadeer R, Akhtar S. *Turk J Chem* 2005; 29: 95.
- [7] Ricordel S, Taha S, Cisse I, Dorange G. *Sep Purif Technol* 2001; 24: 389.
- [8] Uzun I, Guzel F. *Turk J Chem* 2000; 24: 291.
- [9] K. Srinivasan, N. Balasubramaniam, TV Ramakrishna, Studies on chromium removal by rice husk carbon, *Indian J. Environ. Health* 30 (4) (1998) 376-387.
- [10] E. Munaf, R. Zein, The use of rice husk for removal of toxic metals from wastewater, *Environ. Technol.* 18 (1970) 359-362.
- [11] M. Ajmal, RAK. Rao, S. Anwar, J. Ahmad, R. Ahmad, Adsorption studies on rice husk: removal and recovery of Cd (II) from wastewater, *Bioresour. Technol.* 86 (2003) 147-149.
- [12] R. Suemitsu, R. Venishi, I. Akashi, M. Nakano, The use of dyestuff-treated rice hulls for removal of heavy metals from waste water, *J. Appl. Polym. Sci.* 31 (1986) 75-83.
- [13] NA. Khan, M.G. Shaaban, Z. Jamil, Chromium removal from wastewater through adsorption process, in: Proc. UM Research Seminar 2003 organized by Institute of Research Management and Consultancy (IPPP), University of Malaya, Kuala Lumpur, 2003.
- [14] D. Mohan, K.P. Singh, Single and multi-component adsorption of Cadmium and zinc using activated carbon derived from bagasse - an agricultural waste, *Water Res.* 36 (2002). 2304-2318.
- [15] NA. Khan, S.I. Ali, S. Ayub, Effect of pH on the removal of chromium (Cr) (VI) by sugar cane bagasse, *Sci. Technol.* 6 (2001) 13-19.
- [16] S. Ayub, S.I. Ali, N.A. Khan, R.A.K. Rao, treatment of wastewater by agricultural waste, *Environ. Prot. Control J.* 2 (1). (1998). 5-8.
- [17] S. Ayub, S.I. Ali, N.A. Khan, study on the removal of Cr(VI) by sugarcane bagasse from wastewater, *Pollut. Res. J.* 2 (2) (2001). 233-237.
- [18] S. Ayub, S.I. Ali, N.A. Khan, Adsorption studies on the low-cost adsorbent for the removal of Cr(VI) from electroplating wastewater, *Environ. Pollut. Control J.* 5 (6) (2002) 10-20.
- [19] M. Ajmal, RAK. Rao, B.A. Siddiqui, Studies on removal and recovery of Cr (VI) from electroplating wastes, *Water Res.* 30 (6) (1996) 1478-1482.
- [20] K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, S. Pattabhi, Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solution, *Bioresour. Technol.* 87 (2003). 129-132.
- [21] K. Selvi, S. Pattabhi, K. Kadirvelu, Removal of Cr (VI) from aqueous solution by adsorption onto activated carbon, *Bioresour. Technol.* 80 (2001). 87-89.
- [22] W.T. Tan, S.T. Ooi, C.K. Lee, Removal of chromium (VI) from solution by coconut husk and palm pressed fibre, *Environ. Technol.* 14 (1993). 277-282.
- [23] NA. Khan, M.G. Shaaban, M.H.A. Hassan, Removal of heavy metal using an inexpensive adsorbent, in: Proc. UM Research Seminar organized by Institute of Research Management and Consultancy (IPPP), University of Malaya, Kuala Lumpur, 2003.
- [24] C. G. Jun, K. Y. Sam, and J. C. Nag, "Application of fly ash as an adsorbent for removal of air and water pollutants," *Applied Sciences*, vol. 8, no. 7, p. 1116, 2018.
- [25] V. P. Suhas, C. N. Suryakant, and J. K. Sunil, "Industrial applications of fly ash: a Review," *International Journal of Science, Engineering and Technology Research*, vol. 2, no. 9, pp. 1659-1663, 2013.
- [26] Abdel-Ghani, N.T.; Hegazy, A.K.; El-Chaghaby, G.A.; Lima, E.C. Factorial experimental design for biosorption of iron and zinc using typha domingensis phytomass. *Desalination* 2009, 249, 343-347.
- [27] L'Hocine, L.; Pitre, M. Quantitative and qualitative optimization of allergen extraction from peanut and selected tree nuts. part 2. optimization of buffer and ionic strength using a full factorial experimental design. *Food Chem.* 2016, 194, 820-827.
- [28] Mohammed Razzaq, A.; Majid, D.L.; Ishak, M.R.; Muwafaq Basheer, U. Mathematical modeling and analysis of tribological properties of AA6063 aluminum alloy reinforced with fly ash by using response surface methodology. *Crystals* 2020, 10, 403.
- [29] Anderson, M.J. A new method for non-parametric multivariate analysis of variance. *Austral Ecol.* 2001, 26, 32-46.
- [30] Crini G., Peindy H.N., Gimbert F., Robert C. *Sep. Purif. Technol.* 53 (2007) 97.
- [31] Zacar M. O., Engil I.A.S. *Bioresour. Technol.* 96 (2005) 791.
- [32] Kannan N., Meenakshisundaram M. *Water Air Soil Pollut.* 138 (2002) 289.
- [33] Corbitt RA. *Standard hand book of environmental engineering* 2nd ed. McGraw Hill; 1999.
- [34] Bailey S.E., Olin T.J., Bricka R.M. and Adrian D.D. (1999). *Water Research*, V.33(11), pp. 2469-2479.
- [35] Bayat, B. Combined Removal of Zinc (II) and Cadmium (II) from Aqueous Solutions by Adsorption onto High-Calcium Turkish Fly Ash. *Water, Air, & Soil Pollution.* 136, 69-92 (2002).
- [36] Onundi, Y.B., Mamun, A.A., Khatib, M.F.A. et al. Heavy metals removal from synthetic wastewater by a novel nano-size composite adsorbent. *Int. J. Environ. Sci. Technol.* 8, 799-806.

