

# Competitive effects for the adsorption of copper, cadmium and lead ions using modified activated carbon from bamboo

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**Abstract.** Modified activated carbon from bamboo was used as a low-cost potential adsorbent to remove cadmium, copper and lead in single, bimetal and trimetal aqueous solutions. Using the initial concentration of 40 ppm, the analysis was conducted to determine the effect of pH (2.5, 3.0, and 5.5), contact time (60, 90, 120 min) and adsorbent dosage (20, 40, 60 mg/50 mL of solution). Results showed that for single metal aqueous solution, the % adsorption for Cu, Cd, and Pb were 89.0%, 87.4%, and 99.5% respectively. For bimetal aqueous solution the % adsorption of CuCd, CuPb, CdCu, CdPb, PbCu, and PbCd were 90.6%, 98.9%, 55.1%, 80.7%, 99.6%, and 96.05%, respectively. While for trimetal aqueous solutions, % adsorption of Cu, Cd, and Pb were 87.4%, 73.0%, and 98.4%, respectively. The % removal uptake followed the order Pb > Cu > Cd gave insights into competition effects among the three solutes during the adsorption process. Using Box–Behnken Design, the effect pH of the aqueous solution is an important controlling parameter in which the % adsorption increased as the pH level is increased while other parameters were insignificant.

## 1 Introduction

Water pollution by heavy metals discharged from industrial effluents has become a worldwide problem during recent years, as most heavy metal species have toxic effects on organisms and accumulate in biota which does not undergo biological decay thus they are much harder to remove [1].

The long-term use of wastewater in agricultural land results in the contamination of soils by toxic heavy metals. These heavy metals include: zinc (Zn), cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), manganese (Mn), iron (Fe), mercury (Hg), and chromium (Cr) [2,3]. Various toxic heavy metals affect the production and quality of crops and potentially influence the quality of water bodies. It threatens the life of terrestrial, aquatic animals and health of humans by food chain cycle [4,5]. But, the most severe is the kind of pollution it can produce in a long-term and non-reversible.

Hence, to be able to sustain the water, there is a need for careful and planned management. To address the negative impacts it may arise, the use of activated carbon for adsorption of toxic heavy metals can respond to this problem.

Today, activated carbon is a multibillion-dollar manufacturing industry and researchers are continue developing this using local materials. The long-term availability of coal, environmental impacts and potentially increasing cost have encouraged researchers to find an alternative that is cost effective and equally potential. Activated carbon can be manufactured from any organic material that has reasonable elemental

carbon content. Any lignocellulose material can be converted to an activated carbon [6].

This research produced a modified activated carbon from local bamboo using two-step carbonization and impregnation process. The optimal parameters for the adsorption of heavy metals at different operating conditions in a single metal, bimetal and trimetal solutions were evaluated using Box-Behnken Design (BBD).

## 2 Materials and methods

### 2.1 Preparation of the adsorbents

A phosphoric acid were prepared in the ratio of 60:40 phosphoric acids and water [7]. This mixture was mixed thoroughly in a 40:60 ratio with bamboo feedstock (> 4.00 in) and allowed to undergo hydrolysis overnight. The hydrolyzed solid was burned at 100°C for half hour followed by 400 °C for one hour to produce a good quality char. The produced carbon char was ground with a mortar and pestle and sieved to a workable particle size range of 70-100 mesh .The char was washed with 0.1 M HCl and kept in a desiccator for a day to ensure that no air is absorbed. The char/chemical activating agent mixture was prepared to fill roughly the 30% of the beaker volume. For large scale activation conducted to obtain the mass balance, the activating agent was added to the char in a 3:1 char: activating agent (KOH) ratio with impregnation time of 24 hours [7-10]. The resulting

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mixture was mixed in beaker with a mass of distilled water less than or equal to the mass of the carbon char until a paste like mixture was formed. The samples were kept in the furnace for a process hold time of 1 hour at a process temperature of 800°C [10-12]. KOH activation process was used after it was heated. The activated mixtures were transferred and washed in a Buchner funnel to remove the potassium from the carbon. Each sample was washed with 1 L of distilled water [8]. The carbon was then kept in desiccators overnight to dry. After drying, it was weighed to determine the process yield and put in sealed dry polyethene bags.

## 2.2 Preparation of metal concentrations

For a single metal, aliquots of 50 ml of Pb, Cu, and Cd aqueous solutions of 40 ppm concentration were prepared separately. For bimetal combination, aliquots of 50 ml of Pb and Cd, Cd and Cu, and Cu and Pb aqueous solutions with a 50:50 volume ratio of metal were prepared separately. Aliquots of 50 ml for a trimetal combination are being prepared with a volume ratio of 1/3:1/3:1/3 for Pb, Cu, and Cd.

## 2.3 Preparation of samples

Batch adsorption was performed at a room temperature. A mass of 20 mg, 40 mg, and 60 mg of adsorbate was added to each metal solutions of 50 ml [12-14]. The pH of each solution was adjusted to 2.5, 4.0 and 5.5 by adding a few drops of NaOH or HCl solution (prior to the addition of the adsorbent) [14-16]. The flasks were capped and shaken in an agitator at 100 rpm for at different contact time of 60 min, 90 min and 120 min to attain the equilibrium condition [11, 17]. Then, the solutions above was be filtered and the residual metal concentration was determined using the Atomic Absorption Spectrophotometer.

The main parameters derived from the adsorption experiments were % removal or adsorption capacity of copper, cadmium and lead. The percent removal of heavy metal ions will be calculated according to Eq. (1).

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where  $C_0$  = heavy metal initial concentration,  $C_e$  = heavy metal final concentration

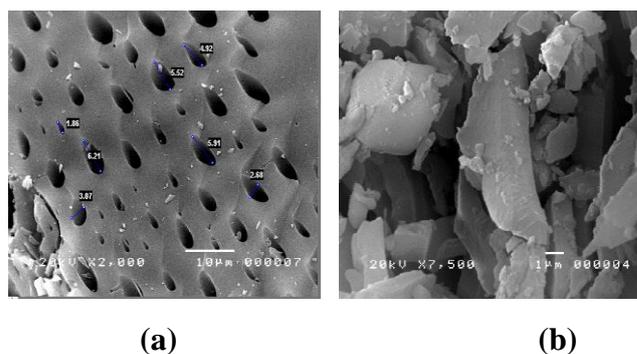
## 2.4 Statistical design

The experimental data were analyzed using a statistical software Design Expert 8 using Response Surface Design to study the variables that may affect the results of the study. The optimum conditions were evaluated using BBD.

## 3 Results and discussion

### 3.1. Characterization of the bamboo char

The surfaces of the modified raw material (Fig. 1) showed cavities, pores, few cracks or voids and more rough surfaces on the activated carbon. Different sizes of granular pores and cavities were produced that increased the surface area of the adsorbent. High porosity was observed on the external surface of the bamboo char. These pores resulted from the evaporation of the chemical reagent ( $H_3PO_4$ ) during carbonization, leaving empty spaces which can hold more solute from solution during adsorption [18,19].



**Figure 1.** SEM image of KOH activated carbon at (a) 2000 and (b) 7500 magnification.

### 3.2. Effects of pH

#### 3.2.1. Single metal

Based from Fig. 2a, it can be observed that increasing the pH increased the % adsorption of Cu, Cd, and Pb for mono component adsorption also increased. A higher percentage of adsorption of the metal ions can be achieved by increasing the pH level of the solution up to 5.5. It can be seen that Pb exhibits higher % removal than Cu and Cd. The highest removal was achieved at pH value of 5.5 having the % adsorption for Cu, Cd, and Pb as 89.0%, 87.4%, and 99.5% respectively.

#### 3.2.2. Bimetal

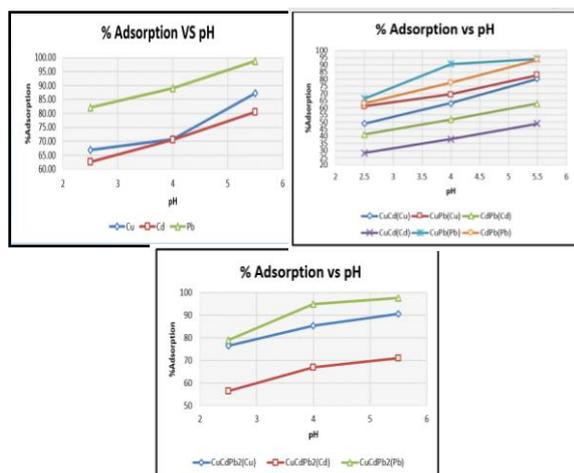
Fig. 2b showed that the % adsorption in bimetallic solutions increased as the pH level was increased from 2.5 to 5.5. The highest % adsorption of CuPb in a bimetallic solution was shown while CuCd was the least. Peak values was achieved at pH 5.5 at which the % adsorption of CuCd, CuPb, CdCu, CdPb, PbCu, and PbCd were 90.6%, 98.9%, 55.1%, 80.7%, 99.6%, and 96.1% respectively.

#### 3.2.3. Trimetal

The results from Fig. 2c, showed the % removal uptake followed the order of  $Pb > Cu > Cd$  which gave insight into competition effects among the three solutes. The %

adsorption in tri metallic solution increased as the pH level was increased from 2.5 to 5.5. It can also be seen that Pb in multicomponent solute achieved the highest % adsorption and Cd came the least. The Pb was removed with higher % than the other two metals, corresponding to the fact that the Pb has the greatest hydrated radii; moreover Pb had the greatest electronegativity. Since the activated carbon is negatively charged, the potential of the electrostatic adsorption among the three adsorbate increased directly proportional to their electronegativity [15].

Overall, the pH of the aqueous solution is an important controlling parameter in the adsorption process and thus the role of  $H^+$  concentration was examined from samples at different range of pH values [19]. The pH of the samples was limited to 5.5; this is because at pH level beyond 5.5 resulted to the decrease in % adsorption due to the formation of soluble hydroxyl complexes. At low pH values the surface of the adsorbent would be closely associated with hydroxonium ions ( $H_3O^+$ ) by repulsive forces to the surface functional groups, consequently decreased the % removal of the metal. When the pH of the adsorbing medium was increased from 2.5 to 5.5, there was an increase in the deprotonation of the adsorbent surface, leading to a decrease in the hydroxonium ions ( $H_3O^+$ ) on the adsorbent surface. This created more negative charges on the adsorbent surfaces [20,21].



**Figure 2.** Effect of pH on metal adsorption in single, bimetal and trimetal component solution.

### 3.3. Effects of pH

#### 3.3.1. Single metal

In **Fig. 3a**, the data showed that the single metal solutions' average % adsorption of copper, cadmium and lead, varied at different contact times and exhibited different responses at any given parameter of contact time.

Also based on the range selected for the design, best single component metal adsorption was achieved at a

contact time of 90, 90 and 60 min at 89.0%, 97.4% and 99.5% adsorption.

#### 3.3.2. Bimetal

Based from **Fig. 3b**, the range selected for the design, optimum binary component metal adsorption in solutions CuCd(Cu), CuPb(Cu), CuCd(Cd), CdPb(Cd), CuPb(Pb) and CdPb(Pb) was achieved at a contact time of 120, 60, 60, 90, 60 and 90 minutes at which 90.6%, 98.8% 52.1%, 80.7% 99.6% and 98.8% was adsorbed.

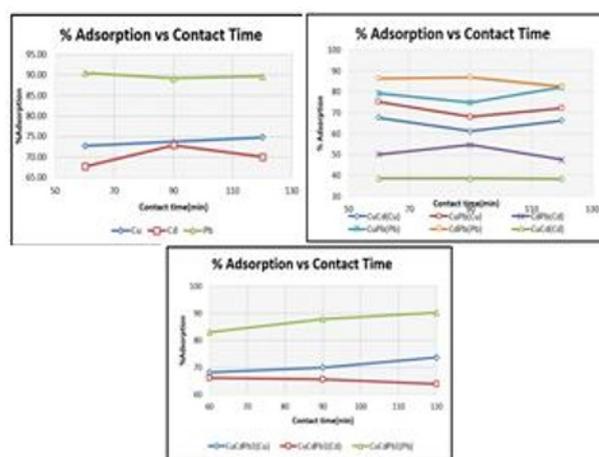
#### 3.3.3. Trimetal

The 73.7% highest adsorption of was shown in **Fig. 3c** obtained for the adsorption of copper, cadmium and lead in trimetal component solutions at contact time of 120 min. A 66.2% adsorption at contact time of 60 min and a 90.3% adsorption at contact time of 120 min were observed.

### 3.4. Effects of dosage

#### 3.4.1. Single metal

In **Fig. 4a**, the data showed that the single metal solutions' average % adsorption of copper, cadmium and lead, varied at different carbon dosages exhibited different responses at any given parameter of carbon dosage. Based on the range selected for the design, optimum single component metal adsorption for copper, cadmium and lead was achieved at a carbon dosage of 0.02, 0.06, 0.04 with 89.0%, 97.4% and 99.5% adsorbed.



**Figure 3.** Effect of contact time on metal adsorption in single, bimetal and trimetal component solution.

#### 3.4.2. Bimetal

From **Fig. 4b** showed the optimum binary component metal adsorption for copper, cadmium, and lead in CuCd(Cu), CuPb(Cu), CuCd(Cd), CdPb(Cd), CuPb(Pb) and CdPb(Pb) was achieved at a carbon dosage of 0.04, 0.06, 0.04, 0.06, 0.04 and 0.02 having 90.6%, 98.8%,

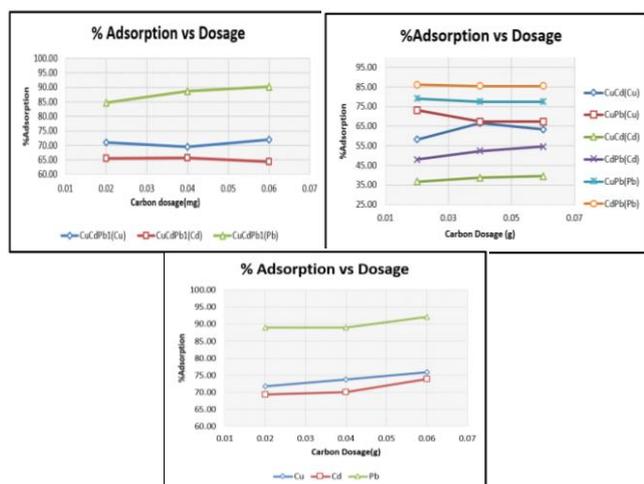
52.1%, 80.7%, 99.6% and 98.8% of metal ions was adsorbed.

### 3.4.3. Trimetal

Based from **Fig.4c** the range selected for the single component metal adsorption for copper, cadmium and lead in a trimetal solution of CuCdPb was achieved at a carbon dosage of 0.04, 0.04, and 0.06 at which 87.4%, 73.0% and 95.9% was adsorbed.

## 3.5. Interactions

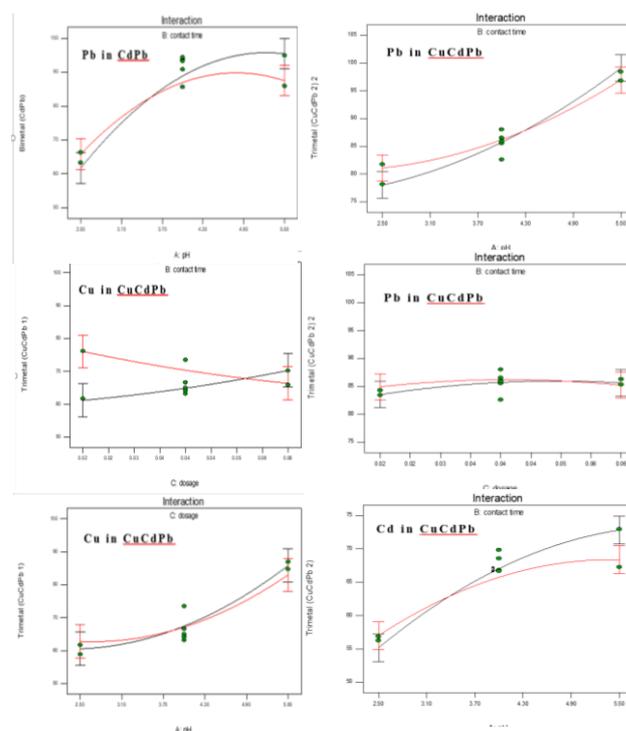
It can be observed from **Fig. 5** the interactions of different parameters on each graph. Figure 5-a illustrated the % adsorption as response in Pb in CdPb solution with fixed carbon dosage of 0.04 at varying parameters of pH and contact time are dependent to one another. The % adsorption of lead in CdPb solution increased with increasing pH at contact time of 60 min. In **Fig. 5b**, the



**Figure 4.** Effect of dosage on metal adsorption in single, bimetal and trimetal component solution.

dosage has an effect on time in the adsorption of Cu in a multicomponent solute in a solution. Increase in dosage yielded an increase in the % adsorption at 60 min while the mean response (% adsorption) at maximum time of 120 min decreased. At increasing time of contact of 120 min, a great decreased of pH 5.5 was observed. For **Fig. 5c**, increasing the pH from 2.5 to 5.5 yielded an increase in the % adsorption at minimum dosage of 0.02 grams while the mean response (% adsorption) at maximum dosage of 0.06 grams decreased the at pH 5.5. In **Fig. 5d**, the % adsorption was slightly lowered by increasing the pH at a time of 120 min as compared to minimum time of 60 min. In **Fig. 5-e** interactions between dosage and contact time at points along 0.05 to 0.06. It can be observed from **Fig. 5-f**, that the pH has a significant effect over time in the adsorption of Cd in multicomponent solution. Increasing the pH from 2.5 to 5.5 yielded a higher % adsorption at minimum contact

time of 60 min, while the mean response (percent adsorption) at maximum time of 120 min was greatly decreased at pH 5.5.



**Figure 5.** Interaction between pH, contact time and dosage.

## 4 Conclusion

The adsorption characteristics of the modified activated carbon from bamboo were tested using aqueous solutions from a single metal, bimetal and trimetal solutions. Results showed that for single metal aqueous solution, % adsorption for Cu, Cd, and Pb were 89.0%, 87.4%, and 99.5% respectively. For bimetal aqueous solution the % adsorption of CuCd, CuPb, CdCu, CdPb, PbCu and PbCd were 90.6%, 98.9%, 55.1%, 80.7%, 99.6%, and 96.1% respectively. While for trimetallic aqueous solution, the % adsorption of Cu, Cd, and Pb was 87.4%, 73.0%, and 98.4% respectively. The results of these experiments showed that the order of Pb > Cu > Cd gave an insight in the competition effects among the three solutes during the adsorption process. Adsorption capacities in the mixture were reduced from their single-solute values for all metals. Using BBD, the % adsorption increased as the pH values increased from 2.5 to 5.5. While the contact time and carbon dosage showed insignificance. At any point within the range of these two parameters does not affect the optimum % removal of the heavy metals. In terms of optimal parameters Cu, Cd, and Pb were validated with a % error of 2.4%, 2.2%, and 1.6% respectively. This means that the efficiency of the optimization process was acceptable.

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