

REMOVAL OF HEAVY METALS USING BANANA FRONS AS ADSORBENT (Cr & Cu)

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Abstract—The use of banana leaves as a one of the bio-waste adsorbent was studied to find its effectiveness removing chromium and copper ions from simulated solutions. Eight types of adsorbent were prepared through physical and chemical treatments with four adsorbents for each treatment consist of 1 non-calcined and 3 calcined at different temperatures. Banana leaves for removing Cr and Cu ions were investigated as function of dose, contact time and initial concentration. The most effective adsorbent for the removal chromium ions was 86.92% by CCT350 (1.0g dose, 50ppm/100ml and 120 minutes), while for the copper ions CPT550 adsorbent was capable to remove until 98.53% adsorbent at the condition 50ml/50ppm of copper ions solution, 0.5g adsorbent and 30 minutes' agitation.

Keywords— *Banana leaves, bio-waste, chromium, copper, adsorption.*

I. INTRODUCTION

High development of manufacturing industries can directly cause uncontrolled discharge of waste that may consequence to water pollution. The waste sources that came from electroplating, pigment, printing, fertilizer, batteries, textile, nuclear power and thermoplastic industries are the examples industries that need the utmost attention since their waste are dominant with heavy metals[1]–[3]. Heavy metals such as Pb, Cd, Zn, Hg, Cr, Cu, Fe, etc. are referred as any metallic element that contain a high relative density and may toxic even at low concentration [4]. Environment Quality (Industrial Effluent) Regulation 2009 have listed the acceptable condition for the industries to compliance before release from the factories.

Previous studies had introduced several techniques in controlling and removing heavy metals from wastewater such as chemical precipitation, ion exchange, coagulation & flocculation, membrane filtration, photo catalysis and adsorption [5], [6]. However, every method has the pros and cons which similar to these current removal techniques. Table 1 shows the advantages and disadvantages of several current heavy metals removal techniques. Out of these techniques', adsorption using activated carbon was the most effective to remove heavy metal from the industrial effluent. However, due to the high cost preparation of commercial activated carbon as adsorbent many new adsorbents that derived from bio-wastes have been introduced to replace the activated carbon adsorbent in removing heavy metals [7]. In addition, other than long time period preparation, the activating agent that used from previous studies to activate the banana leaves quite hazardous to human health.

Previous study had achieved 94.5% removal of copper (II) ions by using activated carbon made from banana leaves [1]. Coffee Husk has been used as an adsorbent to remove Cr(VI) in batch experiment by who reported that 98.1% chromium ions were removed when 1g/100ml of activated carbon, 80ppm of stock solution pH 2 and 60 minutes' contact time [8]. The Aloe Vera leaf has been reported by [9] as one of adsorbent that capable to remove more than 75.5% of copper ions at the condition 120 minutes, 20ppm and 2g of adsorbents. Chromium (VI) removal was 85% at condition of 200mg/L chromium concentration, 1g adsorbent dosage and 60 minutes' contact time using Banana Sheath Fiber (BSH) by [10]. [11] have been studied the effectiveness of Prosopis Juliflora plant in removing Cu (II) and Zinc ions. The maximum of removal for Cu (II) and zinc ions were 96.76% and 96.26% at the condition 50mg/L initial concentration, 5g of adsorbent dose and 90 minutes' contact time.

Table 1: The advantages and disadvantages of several techniques to remove heavy metal ions from waste

Heavy metal removal techniques	Advantages	Disadvantages	References
Chemical precipitation	Simple, inexpensive cost and non-metal selective	Require large amount of chemicals to reduce metals	[12]–[15]
Ion exchange	Metal selective	High maintenance cost	
Adsorption using commercial activated carbon	High efficiency	High cost preparing activated carbon	
Photo catalysis	Able to remove metal and organic pollutant	Long-time operation	[5]
Membrane filtrations	Less chemical consumption	pH sensitive High cost	[12]

In the present study, an attempt has been made to utilize the yellow-green banana fronds to be as agricultural waste adsorbents in removing heavy metals of copper and chromium ions. Even though, previous study has been used banana leaves to remove these heavy metals, but not evidence that the previous researcher

used the banana leaves that classified as bio-waste as adsorbents to remove copper and chromium from simulated wastewater. In addition, other than long time preparation of adsorbents, previous researcher also had used quite hazardous chemical in activating the adsorbent such as $ZnCl_2$ [1], [16] and KOH [17]. Hence, this research more focusing to test the potential and effectiveness of this bio-waste in removal copper and chromium ions using adsorbents that prepared through physical and chemical treatment which involved of less hazardous and low cost chemical substance.

II. METHODOLOGY

A. Biosorbent Preparation (Physical Treatment Adsorbent, PTA)

The banana leaves used in this study was obtained locally. The leaves were washed with distilled water and cut into 1-3 cm sizes [18]. The leaves were dried at $70^\circ C$ for 24 hours in dried oven (Froilabo). The crisp leaves then were grinded and sieved using laboratory test sieve (Endecotts) into 300 Mic. size of powder [19]. The powder of adsorbents was divided into four parts which the first part was kept in air tight plastic and labelled as uncalcined physical treatment adsorbent (UCPT). While, other three parts were calcined in furnace at three different temperatures ($350^\circ C$, $450^\circ C$ and $550^\circ C$). All calcined adsorbents were kept in air tight plastic separately and labelled based on carbonized temperatures (CPT350, CPT450 and CPT550).

B. Biosorbent Preparation (Chemical Treatment Adsorbent, CTA)

The local banana leaves were washed, cut and dried at $70^\circ C$ for 24 hours in dried oven. The dried leaves were grinded roughly using waring blander (04241-11 series) and soaked in acetic acid or vinegar (Tesco) that sold in store until the leaves completely sink in the vinegar solution. The leaves were filter and dried for the second time at $105^\circ C$ (15 hours). After drying process, the pH of the adsorbents was adjusted using 0.1M Sodium Hydroxide and distilled water until within the range 6.5-7.5 [19]. The leaves were dried for last time to remove all the excess water in the adsorbent at the condition $105^\circ C$ for 24 hours [19]. Then, the dried adsorbents were grinded and sieves as PTA.

Similar to PTA also, the powder adsorbents were divided into four parts and the first part was kept in airtight plastic (labelled as uncalcined physical treatment adsorbent, UCCT). While, other three parts were calcined in furnace at the temperature $350^\circ C$, $450^\circ C$ and $550^\circ C$ similar to PTA. All of these calcined adsorbents, were kept in airtight plastic separately and labelled based on carbonization temperature respectively (CCT350, CCT450 and CCT550).



Figure 1: Washing



Figure 2: Sizing



Figure 3: Drying



Figure 4: Soaking with vinegar



Figure 5: Calcination



Figure 6: After drying process



Figure 7: Sieving



Figure 8: Grinding

C. Preparation of Solution

The simulated stock solution of chromium ions (1000mg/L) was prepared by dissolving 2.83g of Potassium Dichromate, $K_2Cr_2O_7$ in distilled water. While, for the preparation 1000mg/L copper ions, 5.66g of Copper Sulphate Pentahydrate, $CuSO_4 \cdot 5H_2O$ was used to dilute with distilled water. Both stock solutions were then diluted with distilled water to obtained desired concentration.



Figure 9: 1000ppm Chromium ions stock solution

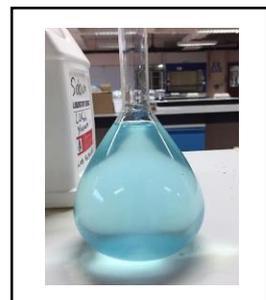


Figure 10: 1000ppm Copper ions stock solution

D. Batch Studies

0.5g of adsorbent powder was placed inside 50 ml metal ions solution in Erlenmeyer flask by placing it in hot plate for the agitation purposed at 700rpm. Sample were taken out at specific duration of time and centrifuged at 1000 rpm for 15 minutes [20]. The supernatant liquid was separated from the residue metal ions and the concentration was analysed by using Atomic Adsorption

Spectrometer. The characterization of adsorbents functional group and porosity were identified using Fourier Transform Infrared Spectrophotometer (FT-IR) and Brunauer-Emmett-Teller (BET).

The percentage removal of Cr & Cu was calculated using equation below:

$$\text{percentage removal (\%)} = \frac{(C_o - C_e)}{C_o} \times 100$$

Where C_o and C_e are the concentration of chromium ions at initial and at equilibrium condition [17].

III. RESULTS AND DISCUSSION

A. Characterization of adsorbents

The FTIR analysis was carried out in order to identify the functional groups that presence in the banana leaves as adsorbent which may involve in adsorption process. Roughly, the wavelength of adsorbents was within 500/cm to 4000/cm. Major characteristic bands recorded for both treatments has been referred based on [28] included: 3500 to 3800 cm^{-1} indicate N-H, O-H & C-H stretch, 3276 cm^{-1} indicate O-H stretch. Alkane and carboxylic acid groups obtained around 2917 cm^{-1} and 2849 cm^{-1} . Peak at 2369 cm^{-1} & 1734 cm^{-1} show $\text{C}\equiv\text{O}$ and $\text{C}=\text{O}$. While at 1616 cm^{-1} , 1243 cm^{-1} and 1011 cm^{-1} show the $-\text{COO}-$, phenolic hydroxyl group ad C-O. The iodide C-X bend indicate for the bend that less than 667 cm^{-1} .

Based on the figures 11 and 12 which show FTIR analysis, it shows that some of these groups present in selected adsorbents and interact with metal ions. The carboxylic and carboxylate group were identified as main metal-removal agent [21]. Hydroxyl group was also effective toward adsorption rate and contribute to exchange of metal ions [22]. Thus, it can be relating that the metal uptake capacity was depended on the several functional groups present in the adsorbent. Unfortunately, the porosity of adsorbents cannot be identified due to equipment failure.

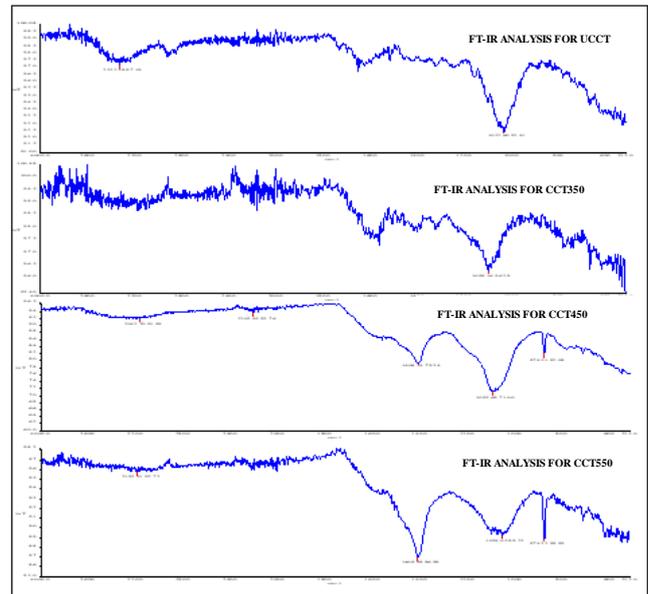


Figure 12: FTIR analysis for chemical treatment adsorbent (CTA)

B. Effect of adsorbents dose on adsorption

Both figures 13 and 14 below indicate the percentage removal of chromium and copper ions against the different amount of dosages used (0.5, 1.0 and 1.5g). Generally, as the amount of adsorbents increase, the percentage removal should be increase [23]. However, several condition cause the removal do not direct proportionally with increase of dosage used.

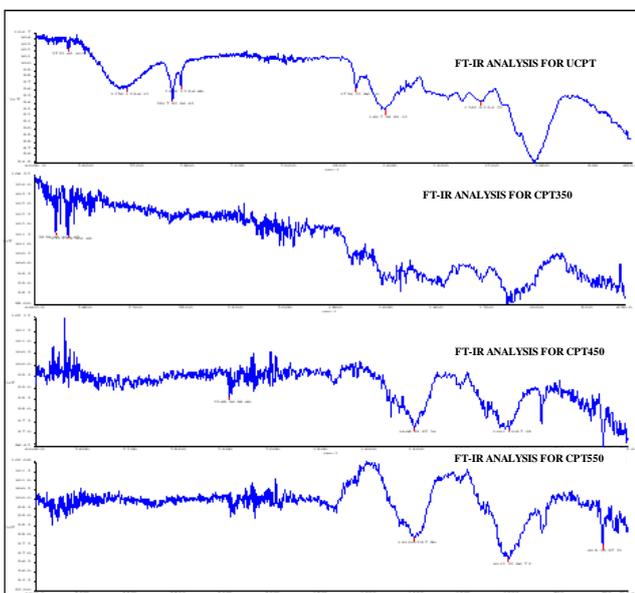


Figure 11: FTIR analysis for physical treatment adsorbent (PTA)

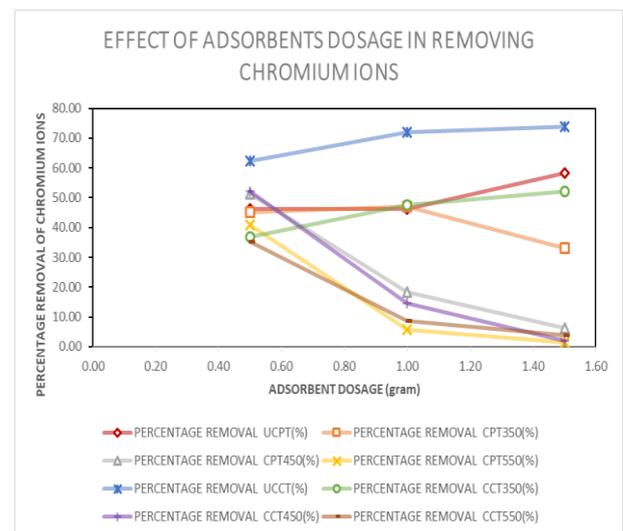


Figure 13: Removal of Cr ions based on different adsorbents dosages

From figure 13, the ranges percentage removal of chromium ions by UCPT were increase from 46% to 58% at 30 minutes when the dosage of UCPT adsorbent increase. However, for the chemical treatment adsorbent, as the dosage of adsorbents (UCCT and CCT350) increase, the removal chromium ions also increase around 62% to 73% and 36 to 52% respectively. Meanwhile, percentage removal of chromium ions by certain calcined adsorbents from chemical and physical were decrease within 30 minutes' contact time. These probably at high temperature, the activated carbon can disrupt the adsorptive bond and decrease the adsorption [27]. Besides that, it also can be consider due to metal shortage in solution at high dosage and possibility due to availability of more adsorption site which was cause plenty of

unoccupied sites as dosage increased [10].

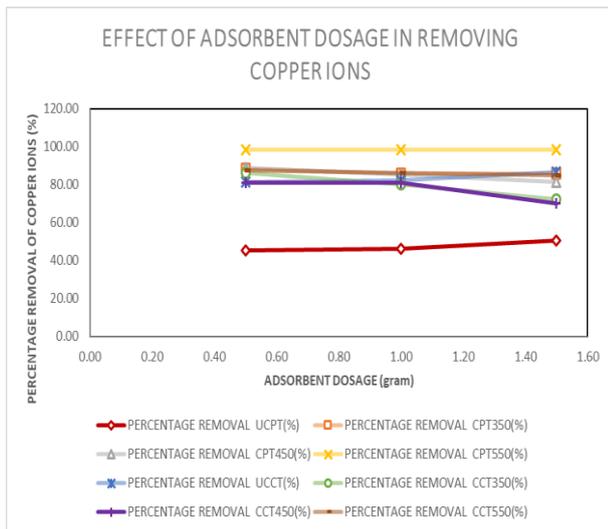


Figure 14: Removal of Cu ions based on different adsorbents dosages

While, figure 14 above shows the result on effect of adsorbent dosages in removing copper ions. Similar in removing chromium ions, as the dosage of UCPT increase, the percentage removal of copper ions also increases from 45% to 50% removal, but for the calcined adsorbent, as the activated carbon dosage increase, the percentage removal was decreased. From the figures 14 also, by varying the dosage of UCCT, CCT350 and CCT450 adsorbent increasingly (0.5g, 1.0g & 1.5g), the percentages removal copper ions were also increase. However, for CCT550 adsorbent, the percentage removal was decrease from 87% to 84% as the dosage varied from 0.5 to 1.5g. These also probably may be due to aggregation or overlapping of the adsorption sites which could led to overall decrease in available binding sites [21], [24], [25].

The maximum percentage removal of chromium ions was 73.92% by UCCT at the condition of 1.5g adsorbent, 50ml of 50ppm chromium solution and 30 minutes' contact time. While 98.53% was the highest percentage removal of copper ions by CPT550 at the dosage of adsorbent 0.5g/50ml, 30 minutes' contact time and 50ppm stock solution.

C. Effect of contact time on adsorption

The longer the contact time, the higher the removal of heavy metal ions since when longer the residence time it means that the more complete adsorption will be occur in the simulated solution [21], [26]. The experiment in determining the effectiveness of the adsorbent against the contact time were conducted within 2 hours. From The both figures 15 and 16, show that as the time increase the removal of metals ions also increase.

From figure 15, CCT350, show the highest removal of chromium ions and UCPT show the lowest removal of chromium ions. Both adsorbents were carried out in same condition of experiment which are 100ml of 50 ppm simulated chromium solution, 120 minutes' contact time and 1.0g adsorbents dosages. Meanwhile, the highest removal for copper ions was CPT550 which shown in figure 16. From the figure also show UCPT as the lowest removal of copper ion. The condition of experiment was conducted similar to the removing chromium ions except the type of the simulated solution which been replace with 50ppm simulated copper ions

solution.

Most adsorbents, at the initial stage were rapid in adsorption of chromium ions but after 1-hour contact time the adsorption become slowly. This pattern similar in removing of chromium and copper ions by physical treatment adsorbent and chemical treatment adsorbent (PTA and CTA) which at beginning the adsorption quite rapid before slowly achieve equilibrium state.

From the figures below also it can be observed that the removal of copper ions seems faster than chromium ion at first 10 minutes' contact time. This probably due to surface of adsorbent which very suit well with size of copper ion compared to chromium ions.

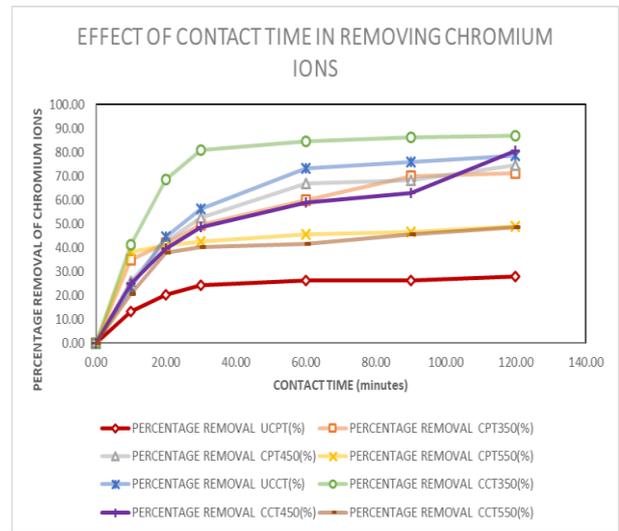


Figure 15: Removal of Cr ions based on different contact time for each kind of adsorbents

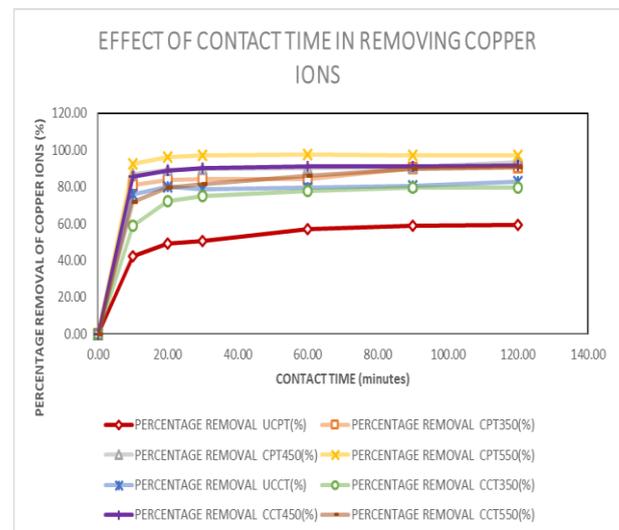


Figure 16: Removal of Cu ions based on different contact time for each kind of adsorbents

Throughout figure 15, the maximum adsorption of chromium ions at the condition of 1.0g/100ml stock solution, 50ppm initial concentration and 2 hours contact time were 86.92% by CCT350. Meanwhile throughout figure 16 the maximum removal of copper ions was 97.45% by CPT550 at the condition of 2 hours contact time, 1.0g/100ml and 50ppm of stock solution.

D. Effect of initial concentration on adsorption

The effect of initial concentration of metal ions on adsorption of chromium and copper ions was studied by varying initial concentration of metal ions from 50ppm, 70ppm and 100ppm. The figures 17 and 18 show that as increase in adsorbate concentration, the removal of metal ions was decrease. The ineffectiveness of the removal metals ions probably due to rapid collision between metal ions. Increase in concentration means that increase the number of ions in the solution which can lead to rapid collision between ions and cause desorption of metals ions from the binding site of adsorbent [21], [24], [26]

Throughout the figure 17, the highest removal of chromium ions was 62.38% by UCCT and the lowest of removal of the chromium ions was 20.53% by CCT550. Both removal was carried out at the condition of 100ppm/50ml chromium solution used with 0.5g adsorbent agitate 30 minutes. While from figure 18, 98.53% and 38.80% were highest and lowest removal of copper ions by CPT550 and UCPT adsorbent. The effectiveness of both adsorbents were identified at the condition 0.5g adsorbents, 30 minutes' contact time and 50 ml of 50 ppm simulated copper solution

IV. CONCLUSION

From the present study, it can be concluded that Banana leaves which classified as bio-waste have a potential to remove the chromium and copper ions in the simulated solution prepared. The carboxylic, carboxylate and hydroxyl group which identified in adsorbents were help in removing of metal ions. However, the level effectiveness of the banana leaves as adsorbent to remove the Cr and Cu ions were depending on the amount of adsorbent dosage used, how long the period for the agitation of adsorbent and simulated solution and different initial concentration of simulated solution was used.

In overall, the most effective removal chromium was 86.92% by CCT350 at condition 1.0g dose, 50ppm/100ml and 120 minutes. While, the most effective adsorbent to remove copper was CPT550 adsorbent with 98.53% removal from 50ml initial concentration of simulated copper ions at the dosage 0.5g, 30 minutes' and 50ppm concentration. Besides that, it also shows that by comparing between uncalcined and calcined adsorbents, the calcined adsorbents from physical and chemical treatments were better in removing heavy metals compared to the uncalcined adsorbents

In addition, between physical and chemical treatments adsorbents, for the removal of chromium ions, chemical treatment adsorbent show more efficient compared to physical treatment adsorbent. The maximum removal of chromium ions by physical treatment adsorbents were only 69.93% by CPT350 adsorbent from 100ml/50ppm of simulated chromium ion with 10g adsorbent dosage and 120 minutes' contact time. While, for removal of copper ions, the physical treatment adsorbents were better than chemical treatment adsorbents within all the parameter conducted since the maximum chemical treatment adsorbents able to achieve only 91.16% by CCT450 from 100ml of 50ppm simulated solution with 1.0g adsorbents dosage and 120 minutes' agitation period.

Thus, banana leaves have been proven to be as adsorbent that capable to remove heavy metals of chromium and copper ions in simulated solution.

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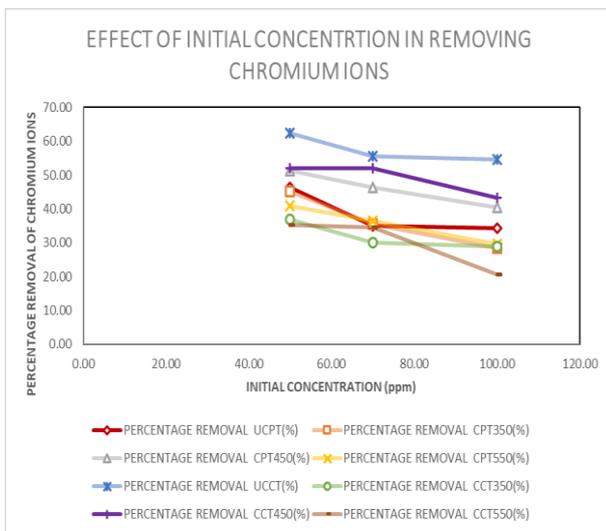


Figure 17: Removal of Cr ions based on different initial concentration of chromium solution for each type of adsorbents

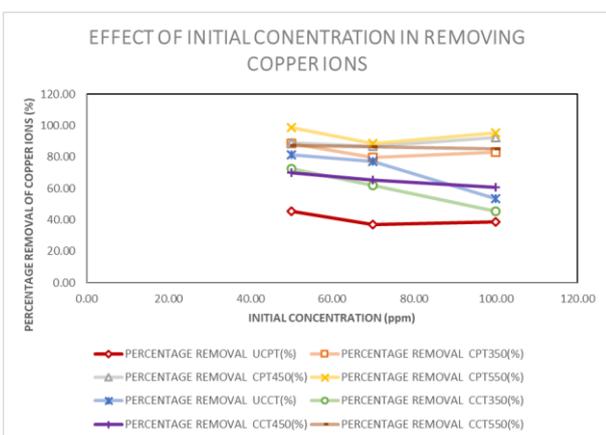


Figure 18: Removal of Cu ions based on different initial concentration of copper solution for each type of adsorbents

