

Removal of Cu(II) from Aqueous Solution using Tea Waste as an Adsorbent

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Abstract – In the present work we investigated adsorption efficiency of tea waste towards the removal of copper. Batch experiment was performed for the removal of copper by using tea waste as adsorbent. Various process parameters studied like effect of bio-sorbent dose, contact time, pH, and effect of various initial copper concentrations. Adsorption methods show the maximum removal of copper was found to be 84% at pH 5 with initial copper concentration, 20 mg/l and 0.5g/100ml tea waste amount use. The equilibrium uptake was attained within 180 min at 30°C temperature. According to experiment result indicate that tea waste could be successfully employed as effective low-cost adsorbents for removal of copper from aqueous solution.

Key Words: Tea waste; Copper; Adsorption; Different parameters; Batch studies;

1. INTRODUCTION

Whole world is now facing waste water contamination problem due to rapid industrialization and urbanization. Metallic ions concentration in water increases the health risks to human and animal due to toxicity of metal. There are at least 20 metals which cannot be degraded or destroyed. One of them is copper (Cu²⁺), 2 mg/l of copper concentration can cause numerous complications. Copper is a toxic metal that present in various industrial wastes. In developing country heavy metal pollution is a serious problem because of huge industrial waste from, galvanizing, metallurgical, electroplating, mining, paints, pigments and pharmaceuticals industry waste that continuously discharge into the environment and natural water stream like river, lake etc. that we use as a domestic and industrial purpose [Kamal Rana et al., 2014; Sureshkumar Halnor et al., 2013]. Water is the most important element for life on earth. Its purest form is colourless, tasteless, and odourless. Increasing toxic levels of industrial effluent raise the importance of water and waste water treatment. Copper ion in small amounts is used in agriculture and copper is an essential element for health of plants, animals and humans. In humans, it helps in the production of blood hemoglobin. However, like any other heavy metal, High concentration of copper creates a kind of disease, which is similar to flu, (Nargawe Tarachand and Dipak, 2016). Copper may be found as a contaminant in food, especially shell fish, liver, mushrooms, nuts and chocolates. Any packaging container using copper material may contaminate the product such as food, water and drink. Copper has been reported to cause neurotoxicity commonly known as "Wilson's disease" due to deposition of copper in the lenticular nucleus of the brain

and kidney failure. In some instances, exposure to copper has resulted in jaundice and enlarged liver. It is suspected to be responsible for one form of metal fume fever. Moreover, continued inhalation of copper-containing sprays is linked to an increase in lung cancer among exposed workers, (A.K. DWIVEDI et. al., 2013). Various method for the removal of copper from wastewater present to recover the metals from our environment and waste water like chemical precipitation method, ion exchange, reverse osmosis, electro-dialysis, electrochemical treatment, membrane separation process and adsorption.

In the present work we used adsorption method because adsorption is found to be one of most alternative process for the removal of copper from wastewater due to its eco-friendly nature and low initial cost. In recent years, various adsorbents have been used for the removal of Cu(II), such as Borasus Flabellifer Coir Powder [Shraddha Rani Singh, and Akhand Pratap Singh, 2012], heavy metal using tea waste [Nargawe Tarachand, and Sharma, 2016], Baobab fruit shell (*Adansonia digitata*) [Hengpeng Ye et al., 2012], rice husk [Naseem Zahra, 2013], Sugarcane Bagasse [Tchoumou M et al., 2015], Using Orange Peel, Sawdust and Bagasse [Ahsan Habib et al., 2007], *Eihhornea crassipies* [C. Pragathiswaran et al., 2013] We need to find an inexpensive and an effective adsorbent to replace commercial methods in removing heavy metals from aqueous effluent [Wiwid Pranata Putra, and Azlan Kamari, 2014]. In current study we used tea waste as an adsorbent for the removal of Cu(II). There are very few companies or societies who buy a very little amount of tea waste that does not have any significant impact. Fibers from tea waste can now be converted into different industrially implemented products like low cost adsorbent during removal of pollutants from waste water [Monoranjan Chowdhury et. al., 2016].

1.1 MATERIALS AND METHODS

Chemicals

All chemicals used in present work were either of analytical reagent (AR) or laboratory reagent (LR) grade. CuSO₄.5H₂O (99%), HCl (98% w/w,) supplied by s.d. fine-chem limited, Distilled water was used in all preparations.

Adsorbent

Tea waste used as an adsorbent for the removal of copper from aqueous solution. Tea waste collected from tea stalls and restaurants of local market in Ujjain India.

Adsorbate

CuSO₄.5H₂O, (analytical grade A.R) were obtained and use as an adsorbate. Synthetic and 1000ppm stock solution prepared for batch experimentation.

Glassware and apparatus used

All glass wares (Conical flasks, Pipette, Measuring cylinders, Beakers, Petri plates and Test tubes etc.) used are of Borosil/Rankem. The instruments and apparatus used throughout the experiment are listed in table-1 and figure-(a) show below:

Table -1: List of Instruments used during the whole experiment.

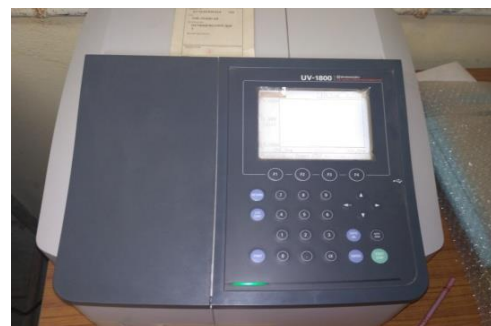
S. No.	Instrument	Name of Company
1.	UV-visible spectrophotometer	UV-1800 SHIMADZU, UV SPECTROPHOTOMETER
2.	Digital Weight Balance	Atco Company
3.	What man filter paper no.42	Whatman
4.	Orbital incubator shaker	Remi Instrument,
5.	pH meter	ANALAB Digital pH meter AN ISO 9001 : 2008
6	Hot air oven 142	REMI Instrument, Mumbai
7	Magnetic stirrer	REMI EQUIPMENTS



(b)ANALAB Digital pH meter AN ISO 9001 : 2008



(c) Hot air oven 142



(d) UV-1800 SHIMADZU, UV SPECTROPHOTOMETER



(a) Digital Weight Balance

Fig –(A)- Instruments used during the whole experiment

Preparation of adsorbents

Tea waste used as an bio-sorbents for the removal of copper from waste water. Tea waste collected from tea stalls from local market in Ujjain, India and washed with distilled water 5-6 times up to colour removal. They were washed with distilled water several times in order to remove soluble substances. After colour removal it is dried in sun light for 5 days and then in a hot oven at 95°C for 10 hours. The dried material converted into powder form by mixer grinder and screened to size 150-250 µm. Again this powder dried at 105°C for 6 hours and then stored in air tight polythene bag at room temperature. Now it was ready to use as an adsorbent. The adsorbents after drying were used for

adsorption studies. Finally Prepared bio-sorbents are shown in figure-(b) below.



Figure (b)- Prepared Tea waste bio-sorbent

Preparation of 0.1M HCL AND 0.1M NaOH- 3.65 g Hydrochloric acid and 4 g sodium hydroxide was dissolved in distilled deionized water in a volumetric flask and made up to 1000 ml mark with the distilled deionized water.

Stock solution preparation:

A stock solution of Cu^{+2} (1000 mg L^{-1}) was prepared by dissolving AR grade 3.929 g of $CuSO_4 \cdot 5H_2O$ in 1000 ml distilled water in 1000 ml volumetric flask. It was dissolved by shaking and the volume was made up to the mark. The stock solution was prepared containing 0.5g/L of standard $Cu(II)$. The pH of the solution is checked using pH meter and it is found to be 6.6, Hydrochloric acid and Sodium hydroxide were used to adjust the solution pH. Distilled water was used throughout the experimental studies.



Figure (c)- Prepared stock solution of copper and filtrate obtained sample

1.2 Experimental procedure and data recording

Procedure on copper removal at various pH values;- Synthetic solution (containing 50 mg/l of copper) was prepared from stock solution of copper. Single Distilled water was used to prepare the solutions. 100 ml of the synthetic solution was taken in each 5 different 100 ml plastic bottles. The pH of this solution was adjusted to 2, 3, 4, 5, and 6 using 0.1M HCl and 0.1M NaOH solution. At different pH 2, 3, 4, 5, and 6 for each adsorbent, 4-5 set of experiments were conducted to study the effects of pH on the removal of copper and 0.5 g of biosorbent was added to each of these flasks. Thereafter, these 100 ml plastic bottles were agitated for 3 hr in magnetic stirrer. After 3 hr of agitation, the solutions were filtered through filter paper (whatman no.42,). The filtrate obtained was diluted using distilled water. The analysis of $Cu(II)$ was done by UV spectrophotometer.

Procedure on copper removal at various adsorbent dose;- Synthetic solution (containing 50 mg/l of copper) was prepared from stock solution of copper. Distilled water was used to prepare the solutions. The pH of this solution was adjusted to 5.0 using 0.1M HCl and 0.1M NaOH solution. For each adsorbent, 4 set of experiments were conducted using the adsorbent concentrations of 0.2, 0.4, 0.6, and 0.8 g to study the effects of adsorbent concentration on the removal of copper. 100 ml of the above stated synthetic solution was taken in each of the 5 different 100 ml plastic bottles and was added with amount of the adsorbent as mentioned above. Thereafter, these 5 different 100 ml plastic bottles were agitated for 3 hr in magnetic stirrer. After 3 hr of agitation, the solutions were filtered through filter paper (whatman no.42). The filtrate obtained was diluted using distilled water and analysis of copper (II) was done by UV spectrophotometer.

Procedure on copper removal at various contact times;-

Experiments have been conducted by batch process to study the effect of contact time on the removal of copper. 100 ml of the copper synthetic solution was taken in each of the 4 different 100 ml plastic bottles. The pH of this solution was adjusted to 5.0 using 0.1M HCl and 0.1M NaOH solution. 0.5 g of adsorbent was added to each bottle. Thereafter, these 5 different 100 ml plastic bottles were agitated for 3 hr in magnetic stirrer. After 40 min, bottle numbered 1 was taken out and the solution was filtered through filter. Similarly after every 40 min bottles numbered 2-5 were taken out and solution was filtered. Then the solution was diluted using distilled water and analysis of copper (II) was done by UV spectrophotometer.

Procedure on copper removal at various initial copper concentrations;-

For each adsorbent four set of experiments were conducted at different initial copper concentration to study the effect of initial copper concentration on the removal of copper by batch process. 100 ml of the synthetic solution was taken in each of the four different 100 ml plastic bottles and the pH of this solution was adjusted to 5.0 using 0.1M HCl and 0.1M NaOH solution. The initial copper concentration used was 20, 30, 40, 50 and 60 mg/l. After the addition of 0.5 g tea waste adsorbent in the solution in 100 ml plastic bottles (pH adjusted initially to 5), Thereafter, these 100 ml plastic bottles were agitated for 180 min in magnetic stirrer. After 180 min of agitation, the solutions were filtered through filter paper (whatman no.42). The filtrate obtained was diluted using distilled water and analysis of Cu (II) was done by UV spectrophotometer.

2. RESULTS AND DISCUSSION

Adsorption Experiment procedure:

Batch adsorption experiments were carried out at room temperature by shaking conical flasks containing desired dose of adsorbent in a predetermined concentration of copper metal solution during certain time. Samples were collected at different time interval. The samples were analyzed using an UV spectrophotometer for the remaining copper ion concentration. Experiments were carried out at initial pH value 5. The percent removal of metals from the solution was calculated by the following equation.

$$\% \text{Removal} = [(C_0 - C_i) / C_0] * 100$$

Where, C_0 is the initial metal ion concentration(mg/L),

C_i is the final metal ion concentration in the solution (mg/L).

In this experiment following factor studied.

- ☑ Effect of contact time
- ☑ Effect of pH
- ☑ Effect of adsorbent dose
- ☑ Effect of initial concentration variation

Effect of pH

Variation of pH is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions. It is directly affects the metal solubility and also determines the surface charge. Fig. 1 shows the effect of pH on heavy metals removal efficiencies of tea waste adsorbent. These studies were start at an 50ppm initial metal ions concentration, and constant adsorbent dose 0.5g/100ml of solution and agitation period are 3hr. pH varying for all heavy metal ions in each solution. The percentage adsorption increases with pH to attain a maximum at 5 pH for Cu^{2+} and there after it decreases with further increase in pH. The maximum removals of Cu^{2+} at 5 pH were found to be nearly 82%. It was clear that at pH 5 the metal uptake was more i.e., 82%, so pH 5 was taken as optimum pH for rest of the experiments. The minimum adsorption was observed at low pH may be due the fact that the presence of higher concentration and higher mobility of H^+ ions, on the other hand in the acidic medium due to high solubility and ionization of metal ions. The surface of the adsorbent becomes more positively charged at high H^+ concentration such that the attraction between adsorbents and metal cations is reduced. In reverse with increase in pH the negatively charged surface area becomes more thus facilitating greater metal removal and then at very high pH also the percentage removal decreases. The maximum adsorption was observed within the pH range 4 to 7 which might be due to partial hydrolysis of metal ions.

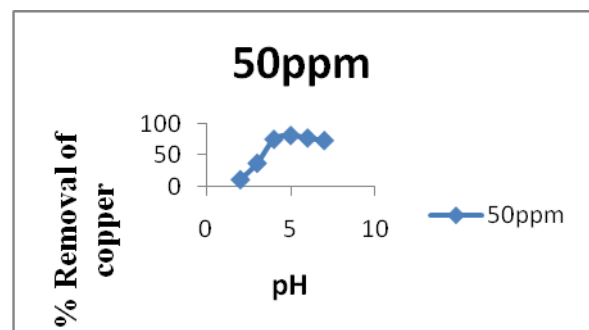


Fig. 1;- Effect of pH on %Removal of copper by tea waste

Effect of contact time

Fig. 2 shows the variation in the percentage removal of heavy metals with contact time using 0.5 g/100mL of tea waste adsorbent at 5 pH. It is observed that maximum removal for Cu (II), ions are nearly 82% at 120 min. contact times. Contact time with increasing removal efficiencies at higher contact time up to 120 min and then gradually decreasing after 120 min. towards 180 minutes. The fast adsorption at the initial stage is probably due to the increased concentration gradient between the adsorbate in solution and adsorbate in the adsorbent as there must be an increased number of vacant sites available at the beginning. The progressive increase in adsorption and, consequently, the attainment of equilibrium adsorption may be due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of tea waste, initially and

subsequently by slower internal mass transfer within the tea waste particles.

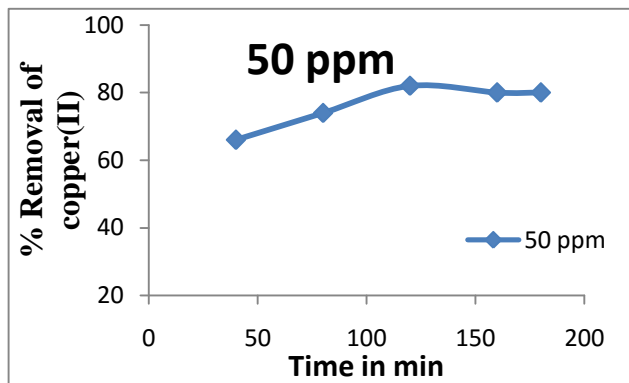


Fig. 2;- Effect of time on %Removal of copper by tea waste

Effect of adsorbent dose

The results for % removal of heavy metals with respect to adsorbent dose over the range 0.2 to 1g/100mL, at pH 5 and 3hr contact time are shown in Fig.3. The percentage removal of heavy metals is seen to increase with adsorbent dose. It can be seen from the figure that the percentage removal initially increases very sharply with the increase in adsorbent dosage, but beyond a value of 0.6 g/100ml, the percentage removal reaches an almost constant value. This may be due to an overlapping of adsorption sites. The maximum removal of Cu is 81% respectively at 0.6 g dose amount of tea waste adsorbent. It is apparent that the percent removal of heavy metals increases rapidly with increase in the dose of the adsorbents due to the greater availability of the exchangeable sites or surface area.

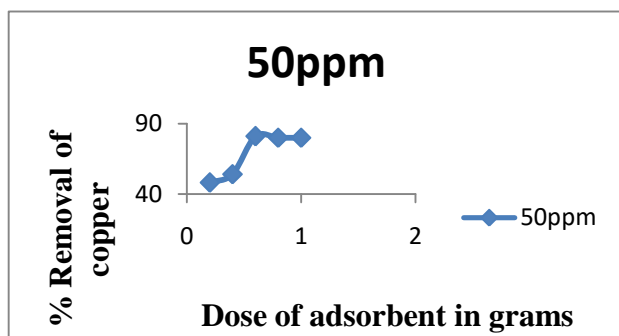


Fig. 3;- Effect of adsorbent dose on %Removal of copper by tea waste

Effect of initial concentration variation;

The effect of concentration at 0.5g/100mL adsorbent dose, 5pH and 180 min. contact time were observed. The initial concentration of copper provides an important driving force to outweigh all mass transfer resistance of metal between the aqueous and solid phases. Removal of Copper for various initial concentrations (20, 30, 50 and 60 mg/L) were observed. The effect of initial concentration on the

percentage removal of heavy metals by tea waste is shown in Fig. 4. It can be seen from the figure-4 that the percentage removal of copper decreases with the increase in initial heavy metal concentration. The percentage removal is highly effective on the 20ppm because maximum 84 percentage removal has been observed for 20 ppm concentration of Cu(II). Initial concentration after which percentage removal decreases gradually to below 84%. At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of the heavy metals ions. Therefore, the fractional adsorption is independent of initial metal ion concentration. However, at maximum concentrations the numbers of heavy metal ions are relatively higher compared to availability of adsorption sites. Hence, the percent removal of heavy metals depends on the initial metal ions concentration and decreases with increase in initial metal ions concentration.

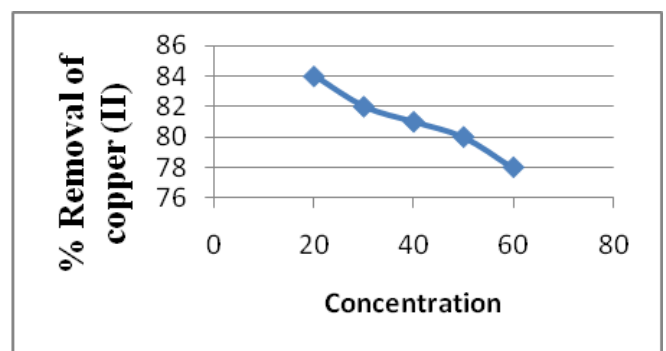


Fig. 4;- Effect of initial concentration on %Removal of copper by tea waste

3. CONCLUSIONS

Tea waste is a cheapest and effective adsorbent for removal of copper ion from waste water. It is observed that in all cases the percentage removal is comparatively lower for initial stage. But in case of initial concentration variation result show that the maximum removal of Cu^{+2} by tea waste at optimum condition (5 pH, 180 min contact time, 0.5 gm/100ml adsorbent dose) is 84% at 20 ppm for the removal of heavy metal ion from waste water. The following conclusions can be drawn from the results of this study:

- ☐ The optimum pH for tea waste is found to be 5 with removal efficiency of 82% at optimum condition (5 pH, 180 min contact time, 0.5 gm/100ml adsorbent dose).
- ☐ The maximum removal of copper found at an adsorbent dosage of 0.6g/100ml for tea waste bio-sorbents, so this can be considered as an optimum dosage at optimum condition (5 pH, 180 min contact time, 0.2-1 gm/100ml adsorbent dose).
- ☐ The optimum contact time is found to be 120 min for tea waste with removal efficiency of 82% at optimum condition (5 pH, different contact time 40 to 180 min., 0.5 gm/100ml adsorbent dose).
- ☐ With an increase in initial Cu (II) ion concentration, % removal of Cu (II) ions by tea waste is found to decrease.

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