

# Removal of Cu(II) Heavy Metal from Aqueous Solution Using Natural Adsorbent - Saw Dust

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## ABSTRACT

*Development of natural adsorbents to treat heavy metal contaminated waste water is a major area of investigation, because of its low cost and eco-friendly nature. In this work the adsorption of copper on pretreated saw dust is studied thoroughly in batch wise. Adsorption efficiency in removal of copper metal ion from aqueous solution has been investigated with various influencing parameters such as pH, contact time, initial concentration and adsorbent doses. The experimental equilibrium parameters were obtained by fitting the experimental data with Langmuir and Freundlich models. This study was done to find a cost effective adsorbent and understand the adsorption process for the adsorption of heavy metal contaminated waste water using the natural adsorbent. The study shows, Langmuir isotherm fits better with experimental data than Freundlich isotherm.*

**Keywords:** *Adsorption, copper (II), Heavy Metal, Sawdust*

## I INTRODUCTION

Heavy metal or Inorganic wastewater from the industries contains harmful metal ions which accumulate in the food chain. The toxic metal ions have great solubility in the aquatic system and thus they can be consumed by living organisms[1]. As they enter the food chain, high concentrations of metal ions may accumulate in the living body. As the metal ions are intake beyond the permitted concentration, they can cause serious health problems[2]. Presence of metal ion pollutants in water cause ecological problems even at very lesser concentration due to its high solubility in aqueous medium. Therefore, it is required to treat the heavy metal contaminated waste water before discharge to the environment. The most widely used methods for removing heavy metals from waste water include ion exchange, chemical precipitation, reverse osmosis, evaporation, membrane filtration and adsorption. Most of these methods suffer from some drawbacks, such as incomplete removal, high capital, and operational cost, disposal of the residual metal sludge, and not suitable for small-scale industries. These facts have been the highlighted factor for an increasing research work related to heavy metals, where the main agenda is to develop new techniques for removal and recovery of these metal species from waste effluents[3], [4].

In recent times, numerous methods have been studied to develop a suitable, cheaper and effective technique that can remove heavy metal effectively. Adsorption process of heavy metal removal is found to be a useful alternate because of its low cost and good metal binding property. Process of adsorption implies the content of an 'adsorbent':- solid that efficiently attaches molecules by means of physical force of adsorption, ion exchange or binding of chemical. The adsorbent available in large amount and of free/low cost are gaining interest. It is important to find and test this kind of materials, as far as the surface characteristics are concern. Agricultural waste products may be an important source of this type of materials for the study of adsorption of heavy metal from waste water containing heavy metal[5].

The use of agricultural waste products for metal binding research has mainly concern on the use of vegetable shells and earthy material, rice bran, corn comb, etc. Majority of the problems have confirmed that use of large amounts of agricultural by-products for the controlling of polluted water is an effective and promising case with a double benefit to the environment. It decreases the residues whose elimination becomes a big, costly problem and it converts the wastes material into useful and inexpensive adsorbents for water treatment[6]. Initially the study of activated carbon was found to be the most popular/effective and widely used synthetic adsorbent in wastewater treatment methodology all over the world. In spite of its systematic use, activated carbon is an expensive material since superior the quality of activated carbon, much costlier it is. Activated carbon requires extra complexing agents to improve removal efficiency. Therefore, it is no longer attractive to use widely in small scale industries because of its high cost[7],[8].

The research interest was directed into production of alternative adsorbents to occupy the place of expensive activated carbon. Focus was moved to the various adsorbents that have metal binding properties, which tend to remove unwanted metals from waste contaminated water at low cost. Because of their low cost and easy availability, bio materials such as zeolites, clay, chitosan, or certain waste materials from industrial operations such as coal, fly ash, and oxides are distinguished as less expensive adsorbents. The main constituents of agricultural waste materials are lignin and cellulose. Other components are hemicellulose, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash and many more compounds that contain a variety of functional groups present in the binding process[9],[10],[11].

Recently, the adsorption process has gained interest as a more promising method for the long term as it is seen to be a more effective and economic approach for heavy metal removal. Adsorption is a fundamental process today due to its flexibility in design and simple operation instead of having to perform adsorptions that are perceived as impractical by most conventional techniques. The advantages of the adsorption process in removing or minimizing the heavy metals even at low concentration enhance the application of adsorption as one practical treatment. Many

research have been done to find adsorption capacity of low cost adsorbents, still more extensive study need to be done on agricultural waste as adsorbents[12], [13].

A review of various processes and adsorbents for heavy metal removal shows that adsorption process has great potential to the elimination of metals from industrial effluents using cheaper adsorbents. More studies should be carried out for low-cost adsorption process to promote large scale use of non-conventional adsorbents. Low cost adsorbents should be used to minimize cost and maximize heavy metal removal efficiency[14], [15]. In this work, natural adsorbents saw dust is investigated to find the removal efficiency of copper heavy metal and effect of different parameters on the removal efficiency.

## **II MATERIALS AND METHODS**

### **2.1 Preparation and Pretreatment of Adsorbent**

Saw dust collected from local carpentry shop and it has many earthly impurities such as stones, mud, sand, dust and also color. This color is a major drawback for setting up or calibrating the spectroscopic instruments which is used to find out the heavy metal ion concentration initially as well as final after adsorption. Hence this color is being removed by first washing it with tap water and then continuously washing it with distilled water until all the color leached into the water. Leaching of color is being increased by adding dilute HCl to the water. Addition of HCl also improves the adsorption efficiency of the adsorbent. Finally it is dried in an oven at  $75 \pm 2^{\circ}\text{C}$ .

### **2.2 Solution preparation for Adsorbate**

Synthetic solutions containing copper have been prepared by dissolving copper sulphate in double distilled water. Solution prepared is of different concentration 1 ppm, 2 ppm, 4 ppm, 6 ppm, 8 ppm and 10 ppm. Cu(II) solutions were prepared by diluting 1000 ppm of  $\text{Cu}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$  stock solution. 100 ml of stock solution was mixed with 900 ml of distilled water to prepare 10 ppm of 1000 ml solution and from that, solution of different desired concentration ranging between 1 ppm to 8 ppm of 100 ml was prepared. The sample was prepared for the calibration as well as experimental study. Samples were hand shaken before analysis so that the settled heavy metal disperses well in the mixture solution and gives accurate concentration level throughout. The pH of the solution was maintained to the required value by adding HCl and NaOH. The prepared solution should be kept air tight so that the solution does not vaporizes due to atmospheric temp and pressure, which may lead in reduction of the desired quantity to be analyzed during the experiment. The compound chemicals used are of analytical grade.

### **2.3 Experimental procedure**

Batch experiments have been conducted by shaking desired amount of the sawdust in 100 ml of the copper solution of required concentration at room temperature. The solution is agitated at 300 rpm for a known period of time. At the end of the determined time the adsorbent is removed by filtration and a sample of the filtrate is found by means of the atomic adsorption spectrophotometer. It should be noted that the pH of the solution in the prepared solution is being treated with the adsorbent where as it is being kept in the shaker at known time intervals and Copper(II) solution was separated by filtration through filter paper.

## **III APPARATUS AND INSTRUMENTATION**

To find out the Cu (II) metal ion of lower concentration Atomic absorption spectrophotometer is to be used, because in UV only the higher color concentration is seen hence we use atomic absorption spectrometer. A calibration curve has been established, preparing standard aqueous solutions of copper (standard) of 1ppm, 2ppm, 4ppm, 6ppm, 8ppm and 10 ppm in order to be able to read the residual concentrations of this metal. The pH measurements have been done with a pH meter. The meter is standardized by the buffer solutions with pH value 3.00, 7.00 and 11.00. Filtration is carried out by the means of the filter paper.

## **IV RESULTS AND DISCUSSION**

### **4.1 Effect of adsorbent dosage**

Adsorption of copper ions on saw dust was studied by varying the adsorbent quantity of 0.3 to 2.4 gm in 100 ml test solution. Tests of adsorption of Cu(II) on sawdust was carried out for different dosages at initial ion concentration of 8ppm and at different agitation time 15 min, 30 min, 45 min and 60 min with agitation speed of 300. Test was conducted at room temperature and sample pH was maintained at 7. At the end of the experiment, sample was filtered and the concentration of Cu(II) was analyzed with the help of Atomic absorption spectrophotometer.

Table 1 to Table 4 shows percentage of heavy metal removal for different dose of adsorbent with contact time of 15 min, 30 min, 45 min and 60 min, respectively. All these tables show that the removal efficiency is increases with increasing adsorption dose. It is evident from Fig.1 that the percentage removal increases slowly till 0.6 gm/ 100 ml dose and later on increases rapidly. At higher adsorption dose percentage removal of metal remain constant. Removal efficiency does not change much beyond adsorption dose 1.8gm/100 ml of sample. The maximum removal was found to be 53% in these specific conditions.

**Table 1: Effect of adsorbent dosage Cu(II) heavy metal adsorption for contact time 15 min**

Adsorbent dosage (gm)	Initial-ion concentration (ppm)	Final-ion concentration (ppm)	% Removal
0.3	8	7.5181	6.0241
0.6	8	6.9880	12.6506
0.9	8	6.0241	24.6988
1.2	8	5.2048	34.9398
1.5	8	4.2410	46.9880
1.8	8	4.0964	48.7952
2.1	8	4.0723	49.0964
2.4	8	3.9759	50.3012

**Table 2: Effect of adsorbent dosage Cu(II) heavy metal adsorption for contact time 30 min**

Adsorbent dosage (gm)	Initial-ion concentration (ppm)	Final-ion concentration (ppm)	% Removal
0.3	8	7.2530	9.3373
0.6	8	6.8675	14.1566
0.9	8	5.6627	29.2169
1.2	8	4.6024	42.4699
1.5	8	3.9759	50.3012
1.8	8	3.9036	51.2048
2.1	8	3.8795	51.5060
2.4	8	3.8554	51.8072

**Table 3: Effect of adsorbent dosage Cu(II) heavy metal adsorption for contact time 45 min**

Adsorbent dosage (gm)	Initial-ion concentration (ppm)	Final-ion concentration (ppm)	% Removal
0.3	8	7.0361	12.0482
0.6	8	6.5060	18.6747
0.9	8	5.4217	32.2289
1.2	8	4.4096	44.8795
1.5	8	3.9036	51.2048
1.8	8	3.8313	52.1084
2.1	8	3.7831	52.7108
2.4	8	3.7590	53.0120

**Table 4: Effect of adsorbent dosage Cu(II) heavy metal adsorption for contact time 60 min**

Adsorbent dosage (gm)	Initial-ion concentration (ppm)	Final-ion concentration (ppm)	% Removal
0.3	8	6.9880	12.6506
0.6	8	6.4578	19.2771
0.9	8	5.3494	33.1325
1.2	8	4.3373	45.7831
1.5	8	3.8554	51.8072
1.8	8	3.8072	52.4096
2.1	8	3.7590	53.0120
2.4	8	3.7349	53.3133

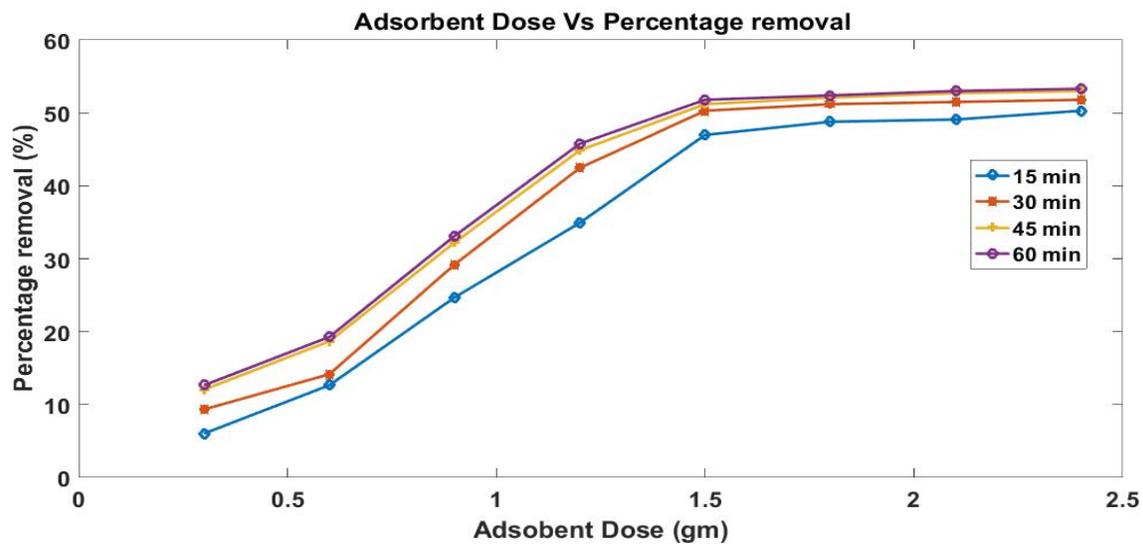


Figure 1: Percentage removal of Cu(II) heavy metal with adsorbent dose (gm/100 ml)

#### 4.2 Effect of agitation/contact time

Contact time is another necessary parameter for an optimal wastewater treatment process. Fig. 2 shows percentage removal of Cu(II) with agitation time for different adsorbent dose. It was found that an increase in agitation time increases removal of heavy metal. It was also observed that the rate of increase of Cu(II) removal is more up to 45 min, which remains almost the same beyond 45 min. The optimal contact time was noted at 45 min. The removal of Cu(II) increased with an increase in shaking speed. An enhanced removal at higher shaking speed is probably due to the decrease in boundary layer thickness surrounding the adsorbent particles.

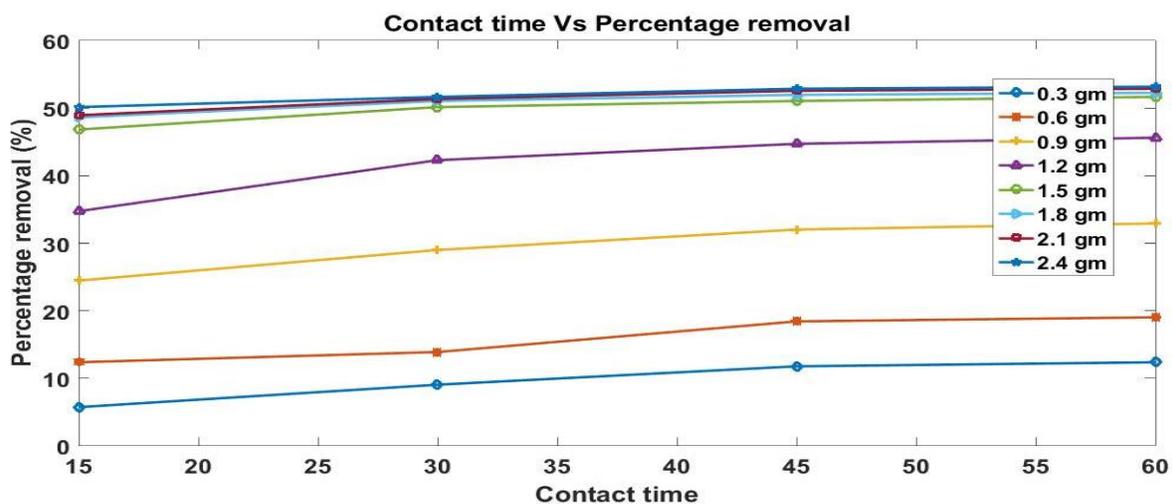


Figure 2: Percentage removal of Cu(II) heavy metal with contact time

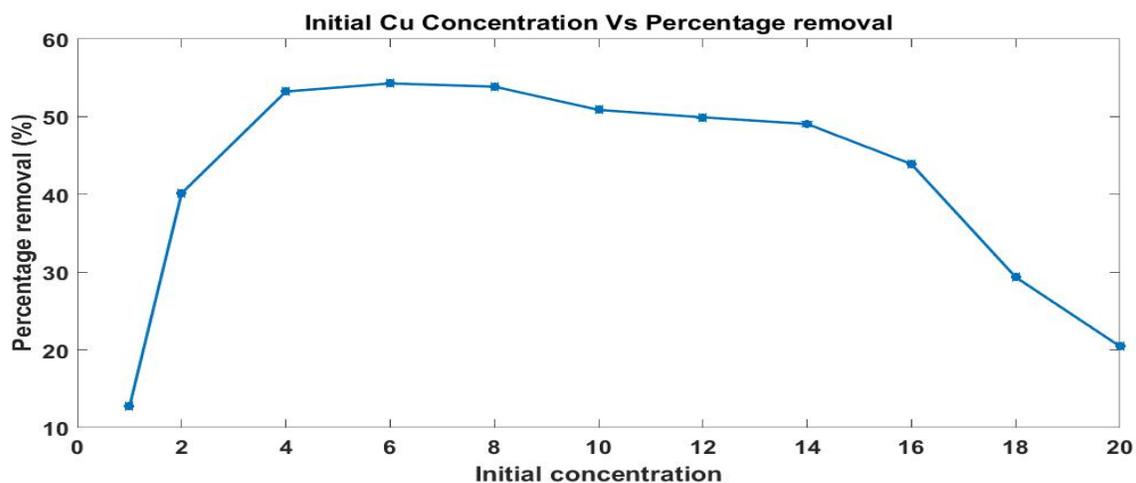


**4.3 Initial ion concentration effect**

Effect of initial ion concentration on heavy metal removal is shown in Table 5. The test was conducted at constant pH of 7 and adsorbent dose of 1.8 gm/100 ml. The percentage removal of copper heavy metal increase initially with increasing copper concentration and shows decrease in removal when Cu(II) concentration reached 8mg/L (see Fig. 3). The maximum removal of heavy metal was observed 54% at the optimal initial ion concentration. The optimal range of initial ion concentration was found to be 6 – 8 ppm. At lower concentrations, copper ion in the solution interacts with empty sites provide better removal efficiency. At higher concentrations, more Cu(II) ions were unadsorbed in solution due to the saturation of sites. The copper adsorption is suited to different mechanisms of metal ion exchange processes. During the metal ion exchange process, copper ion has to go through the pores of the adsorbent surface, but also through channels of the pores.

**Table 5: Effect of initial ion concentration on Cu(II) heavy metal adsorption**

Initial-ion concentration (ppm)	Concentration after adsorption (ppm)	% Removal
1	0.8728	12.7182
2	1.1970	40.1496
4	1.8703	53.2419
6	2.7431	54.2810
8	3.6908	53.8653
10	4.9127	50.8728
12	6.0100	49.9169
14	7.1322	49.0559
16	8.9776	43.8903
18	12.7182	29.3433
20	15.9102	20.4489



**Figure 3: Percentage removal of Cu(II) heavy metal with initial ion concentration**

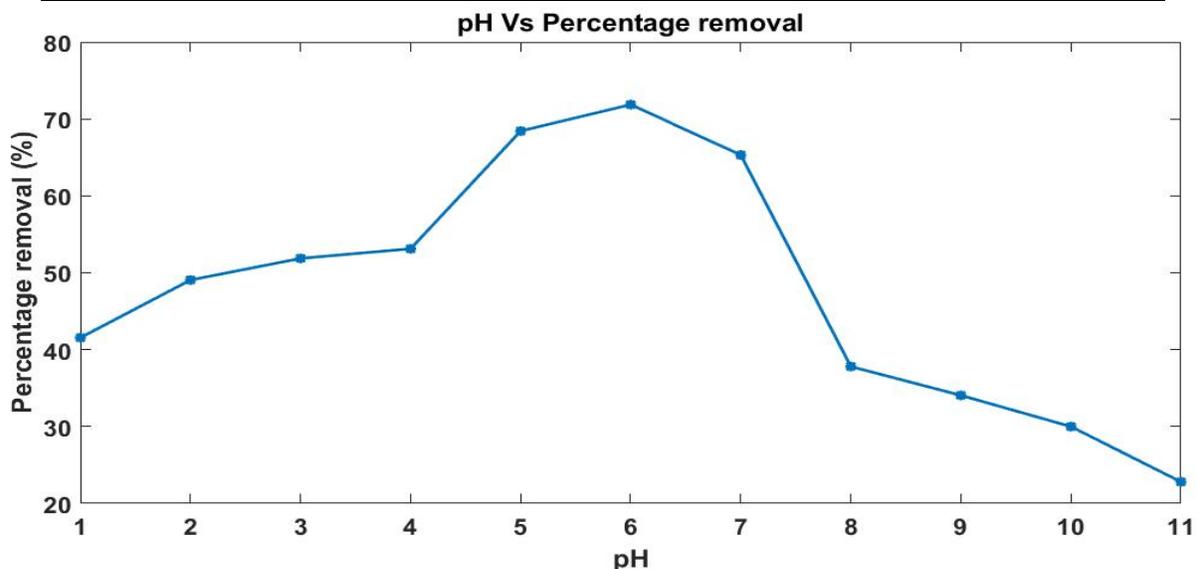


#### 4.4 pH Effect

The pH of aqueous solution is an important parameter in the adsorption process. The effect of pH on heavy metal adsorption was studied by varying medium pH from 1 to 11 and result is shown in Table 6. Other parameters such as agitation time, adsorbent dosage, and initial ion concentration were kept constant. Agitation time, adsorbent dose and initial ion concentration are 45 min, 1.8 gm/100 ml and 8 ppm, respectively. Fig.4 shows that the retention of copper by sawdust increases till pH 6 and then decreases slightly in the range of 8 – 11. The maximum sorption capacity 72% was observed at pH 6 due to the interaction of  $\text{Cu}^{2+}$ ,  $\text{Cu}(\text{OH})^+$  and  $\text{Cu}(\text{OH})_2$  with the surface of the sawdust. Adsorption capacity decreases at high pH may be due to the formation of soluble hydroxy complexes.

**Table 6: Effect of pH on Cu(II) heavy metal adsorption**

Sl.no	pH value adjusted	Initial-ion concentration (ppm)	Concentration after adsorbent (ppm)	% Removal
1	pH1	8	3.3250	41.5625
2	pH2	8	3.9250	49.0625
3	pH3	8	4.1500	51.8750
4	pH4	8	4.2500	53.1250
5	pH5	8	5.4750	68.4375
6	pH6	8	5.7500	71.8750
7	pH7	8	5.2250	65.3125
8	pH8	8	3.0250	37.8125
9	pH9	8	2.7250	34.0625
10	pH10	8	2.4000	30.0000
11	pH11	8	1.8250	22.8125



**Figure 4: Percentage removal of Cu(II) heavy metal with pH on adsorption**



4.5 Adsorption isotherm

Table 7 shows the equilibrium ion concentration and amount of ion adsorbed per unit adsorbent for different initial ion concentration. The Langmuir and Freundlich isotherm models are widely used to describe the experimental data of adsorption isotherm. In this study both isotherm models were used to identify how Cu(II) ions interact with adsorbents. The study was carried out at optimal condition and at room temperature. It was found that Langmuir isotherm fits better than Freundlich (see Fig.5). Square root of error for Langmuir and Freundlich isotherm was found to be 0.116 and 0.173, respectively (see Table 8). The coefficients for both isotherms are shown in the Table 8.

Table 7: Equilibrium ion concentration for different initial ion concentration

Initial ion concentration(ppm)	Equilibrium ion concentration(ppm)	q (mg ion adsorbed/gm adsorbent)
1	0.8728	0.0071
2	1.1970	0.0446
4	1.8703	0.1183
6	2.7431	0.1809
8	3.6908	0.2394
10	4.9127	0.2826
12	6.0100	0.3328
14	7.1322	0.3677
16	8.9776	0.3901
18	12.7182	0.3987
20	15.9102	0.4018

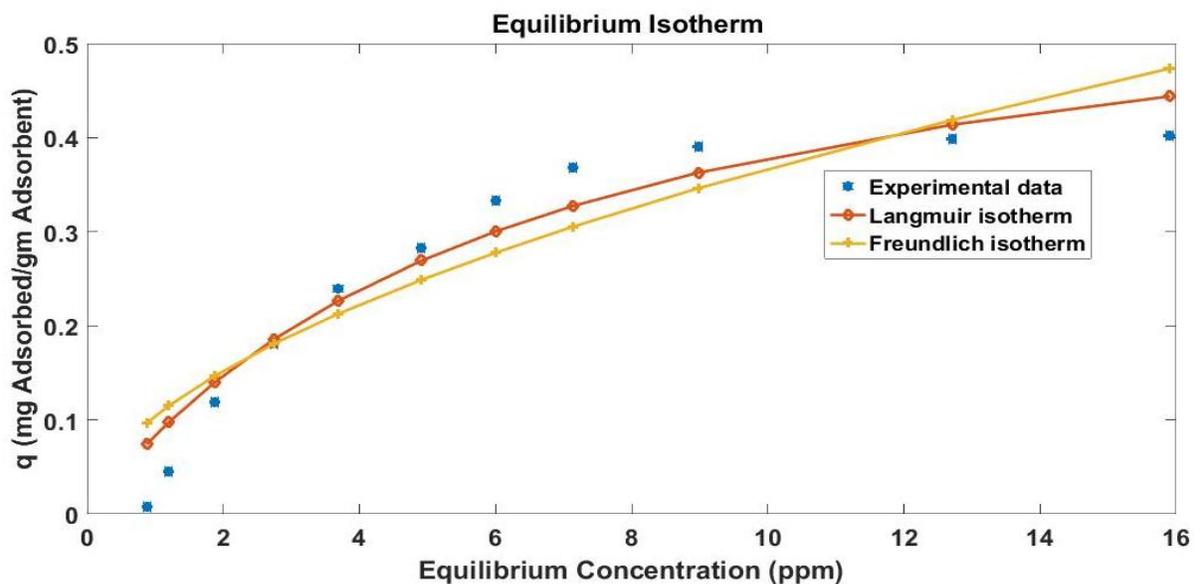


Figure 5: Adsorption Isotherm using Langmuir and Freundlich model

**Table 8: Adsorption isotherm model and model parameters**

Model	Langmuir $q_e = \frac{K q_m C_e}{1 + q_m C_e}$	Freundlich $q_e = K_d C_e^n$
Parameters	$K = 0.154$	$K_d = 0.104$
	$q_m = 0.625$	$n = 1.826$
Square root of error	0.116	0.173

## V CONCLUSIONS

This research work examined the Cu(II) heavy metal removal efficiency from Cu(II) metal ion solution using pretreated saw dust as natural adsorbent. The removal of Cu(II) heavy metal was found to be 72% when some optimal operating conditions were maintained. Optimal adsorbent dose, contact time, initial ion concentration and pH of the sample were observed 1.8 gm/100 ml, 45 min, 8 ppm and pH 6, respectively. In this study it is shown that the experimental data fits more towards Langmuir isotherm model than Freundlich. The natural adsorbent saw dust found to be useful in the removal of Cu(II) heavy metal from metal solution. It is expected to get more efficient removal of heavy metal if surface characteristics of adsorbent are improved.

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