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Economical Wastewater Treatment for Removal of Copper (II) Ions From Wastewater

Deokar G. N.¹, Desale L. R.², Harkal S. P.³

Assistant Professor, Department of Civil Engineering, SNJB's COE, Chandwad, 423101 India

Abstract: Water pollution is one of the major problems faced by the entire world. The industrial and urban development leads to the water pollution due to accumulation of heavy metals in the wastewater. Several techniques have been used such as chemical precipitation, electrolysis, ion exchange etc. to treat such water contaminated with heavy metals. One of the best option is adsorption, which is easier environment friendly method to treat wastewater. By using various natural and agro-based wastes as an adsorbent is useful in reducing cost in adsorption process. An attempt to use natural material like soil with activation and banana peel has made to treat water contaminated with heavy metals. In this study, the copper ions are removed with adsorption by using banana peels and activated soil. The performance of adsorbent is observed by varying different parameters such as pH, adsorbent dose, initial concentration and contact time. It is found that the sufficient removal of Cu ions at optimum parameters like pH, adsorbent dose, initial concentration and contact time is at 5, 2 gm, 5 mg/l and 150 minute respectively for banana peels and 6, 2gm, 5mg/l and 150 minute respectively for activated soil. For all optimum parameters the maximum reduction in metal ions is observed in the range of 70% to 80% for banana peels whereas for activated soil it is 65 % to 75%. The R^2 value in the present analysis is less than one, representing that the adsorption of copper ions onto both the adsorbents is favorable and the equilibrium data also fit well with Langmuir and Freundlich isotherm.

Keywords: Banana peels, activated soil, adsorption, concentration, agro based

I. INTRODUCTION

During the past decades, heavy metals have emerged as a major inorganic pollutant and threat to natural environment and human health. The only solution to protect the environment and human health is their removal from metal laden wastewater before discharging them into aqueous streams.

These metal ions, primarily originate from electroplating, mining & ore processing, paint, chemicals and fertilizer industries and metal surface treatment processes. Among the heavy metals, copper is the major available type of heavy metal in the aquatic environment. The excess copper compound in the body has gastrointestinal effects. During the last few decades, the sustainable removal of heavy metals from water and wastewater has become a prime concern and a major challenge for scientists. Owing to the toxic and adverse effects of heavy metals, most industries are advised to treat wastewaters systematically so that the metal contents can be minimized in their wastes.

Several conventional technologies are in use for heavy metal removal from wastewater. These technologies include chemical precipitation, redox approach, ion exchange, electrolysis, membrane separation and adsorption. Generally, all these treatments lead to certain disadvantages such as incomplete removal of heavy metals, high-energy requirements and production of toxic sludge. Extensive studies have been undertaken for the development of more effective methods in removing metal pollution. Amongst these, adsorption is more reliable and promising owing to its efficiency, local availability of adsorbents, operational simplicity, cost effectiveness and regeneration potential of the adsorbents. Numerous approaches have been studied in recent years in order to find an economic adsorbents for water treatment and heavy metals removing.

II. METHODOLOGY

A. Material Preparation

1) Preparation of Adsorbent

Banana peels from Banana fruits are collected. Banana peels were dried in sunlight for 3 days and cuts into small pieces then washed with distilled water and dried it in oven at 105°C for 5 hours. Oven dried pieces were grounded and sieved using IS sieve.

Soil required for brick manufacturing is collected. The soil sample is oven dried for 24 hrs and then washed with distilled water and diluted hydrochloric acid. Further it is dried in oven at 105°C for 5 to 6 hours.

2) Preparation of Stock Solution

The stock solution 1000 mg/L of Cu(II) ions is prepared by dissolving 3.51g of pure salt $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 1L of distilled water and practiced for all experiments with required dilution.

B. Test on adsorbents

1) pH

Take 10 gm of sample add 100 ml distilled water in it. The sample is transferred to bottle and kept for shaking at 200 rpm for 15 minutes.

The sample is kept still for 15 minutes, then the solution is passed through filter paper. The filtrate so obtained is tested for pH by using digital pH meter.

pH of Banana peel – 5.11

pH of activated soil – 7.65

2) Electrical conductivity

Take 10 gm of sample add 100 ml distilled water in it. The sample is transferred to bottle and kept for shaking at 200 rpm for 15 minutes. The sample is kept still for 15 minutes, then the solution is passed through filter paper. The filtrate so obtained is tested for electrical conductivity by using electrical conductivity meter.

Conductivity of banana peel solution – 3.302 mhos

Conductivity of activated soil solution – 495.3 micromhos

3) Specific gravity

Clean and dry the density bottle. Weigh the empty bottle with stopper (W_1). Take 5 to 10 gm of soil sample which is cooled in desiccator. Transfer it to the bottle. Find the weight of the bottle and soil (W_2). Now add distilled water to the bottle and weigh the bottle filled with soil and water (W_3). Fill the empty bottle with water and weigh it as (W_4)

Specific gravity of soil sample is 2.62

4) Bulk Density

Specific gravity bottle of 25 ml capacity without the stopper was weighed. Then it is filled with the sample up to the edge of the neck tapping the bottle up to 20 times and weighed. The bulk density is obtained by dividing the weight of the sample with volume of the sample.

Bulk density of soil sample is 1.39 gm/ml

5) FTIR Analysis

a) Sample- Banana peels

FTIR spectroscopy was performed to characterize the chemical functional groups of banana peels. These spectra were obtained from scanning in the range of 500- 4000 cm^{-1} . The band of banana peel shifted to 3662.94 cm^{-1} , to 3018.70 cm^{-1} indicating that primary and secondary amines and amides (stretch) groups are involved and also involve H-bonded, carboxylic acids. From the spectra, the results indicate that aldehydes, esters, hydrocarbons, nitro group alkene, aromatic and alkyne are also observed.

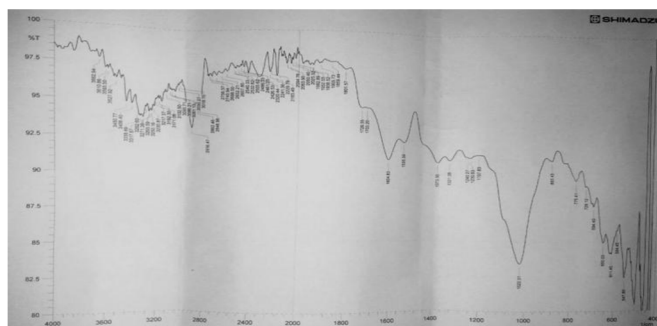


Figure 1 – FTIR spectra of Banana peel

b) Sample – Activated soil

FTIR spectroscopy was performed to characterize the chemical functional groups of activated soil. The band of activated soil shifted to 3626.29 cm⁻¹ to 2920 cm⁻¹ indicating primary and secondary amines and amides (bend), phenols, alcohols, carboxylic acid, H-bonded, aromatic, alkene, bromide and iodide are observed.

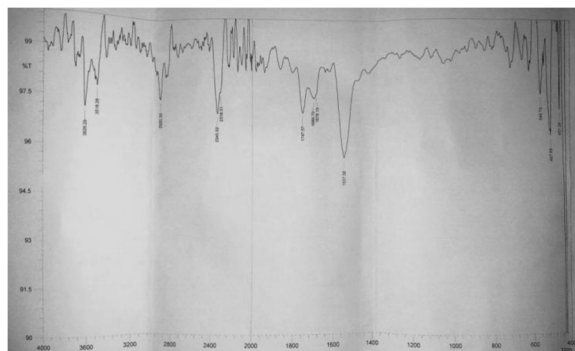


Figure 2 – FTIR spectra of activated soil

6) Wet Chemical Analysis

a) Banana peels

Sr. No.	Details	Observations (%)
1	SiO ₂	14.08
2	Al ₂ O ₃	17.53
3	Fe ₂ O ₃	0.16
4	MgO	0.019
5	SO ₄	0.0028
6	Loss of ignition	82.57

b) Activated soil sample

Sr. No.	Details	Observations (%)
1	SiO ₂	34.36
2	Al ₂ O ₃	19.84
3	Fe ₂ O ₃	5.26
4	MgO	0.56
5	SO ₄	0.0018
6	Loss of ignition	4.94

C. Procedure of work

1) Study of pH

To study the effect of pH on Cu(II) adsorption onto banana peel and activated soil were kept constant at 2g/100 ml, and varying the pH of the samples using 0.1N HCl and 0.1N NaOH between (4 to 8). Each of Cu(II) concentrations were 5 mg/l for all solutions during the experiment. Adsorption studies were carried out at room temperature. The samples were shaken for 90 minute with 220 rpm (this speed was able to mix and reaches to equilibrium), at room in the 125 ml bottle volume and left still for 24 hours. Optimum pH value helps to make the study of effect of other factors, more easier.

2) Study of Adsorbent

The impact of the adsorbent amount on the equilibrium adsorption for each of Cu(II) were investigated with banana peels and activated soil of 0.5,1,1.5, 2 and 2.5g in five sets of 100 ml water, which contained 5 mg/l of Cu(II) concentrations each, at pH 5. The samples were shaken at speed 220 rpm at room temperature for 90 minutes and were left for 24 hours before the water samples filtered and analyzed in terms of Cu(II) and . The same procedure was done with the activated soil as an adsorbent.

3) Study of Initial Concentration

The impact of the initial concentration on the equilibrium adsorption for each of Cu (II) were investigated with banana peels and activated soil of 5, 10, 15, 20, 25 mg/l in five sets of 100 ml water at pH 5. The samples were shaken at 220 rpm at room temperature for 90 minutes and were left for 24 hours before the water samples filtered and analysed in terms of Cu(II) and the same procedure was done with the activated soil as an adsorbent.

4) Study Of Contact Time

The impact of contact time on the equilibrium adsorption for Cu (II) was investigated with banana peels and activated soil for 30, 60, 90, 120 and 150 minute contact time in five sets of 100 ml, which contained 5 mg/l of Cu (II) concentration at pH 5. The samples were shaken at 220 rpm at room temperature for 90 minutes and were left for 24 hours before the water sample filtered and analysed in terms of Cu(II) and the same procedure was done with the activated soil.

5) Study of Equilibrium Isotherm Models

The two models were used to fit the experimental data namely Langmuir model and Freundlich model. Langmuir and Freundlich model were used to describe the adsorption equilibrium.

a) Langmuir Isotherm

Langmuir proposed theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm has found successful application to many other real adsorption processes. The Langmuir isotherm is based on assuming monolayer sorption onto surfaces onto surface with fixed number of well defined sites. The form of Langmuir isotherm is expressed as below :-

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 b C_e}$$

Where q_0 = amount adsorbed on unit mass of the adsorbent in mg/g

Q_0 = adsorption capacity of adsorbent (mg/g)

b = Langmuir constant which is measure of energy of adsorption (l/mg)

C_e = equilibrium concentration in of adsorbate (mg/l)

The values of Langmuir constant (slope) and adsorption capacity (intercept) was obtained from linear correlation plots between $1/q_e$ and $1/C_e$.

The essential characteristics of Langmuir isotherm model can be explained in terms of dimensionless constant separation factor or equilibrium parameter R which is defined by

$$R = \frac{1}{1 + b C_0}$$

Where, b = Langmuir constant, l/mg

C_0 = initial concentration, (mg/l)

b) Freundlich isotherm

Freundlich demonstrated that the ratio of the amount of solute adsorbed onto given mass of adsorbent to the concentration of the solute in the solution was not constant at different solution concentrations. The Freundlich adsorption isotherm is empirical equation used to describe heterogeneous system. So the empirical equation can be written as :-

$$q_e = K_f C_e^{1/n}$$

where q_e = amount adsorbed on unit mass of the adsorbent in mg/g

K_f = Freundlich constant which is related to the adsorption capacity of adsorbent related to the bonding energy

C_e = the equilibrium concentration of adsorbate in solution after adsorption, mg/l

n = Freundlich coefficient

the Freundlich model was chosen to estimate the adsorption intensity of the adsorbent towards the linear form is represented by following equation:-

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

Where K_f = Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, mg/g

$1/n$ = Freundlich intensity parameter

C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/l

For $1/n$ less than unity, adsorption is the predominant process taking place otherwise desorption becomes predominant. The values of Freundlich constants (slope) and adsorption capacity (intercept) were obtained from the linear correlation plots between $\ln q_e$ with $\ln C_e$.

Values of R

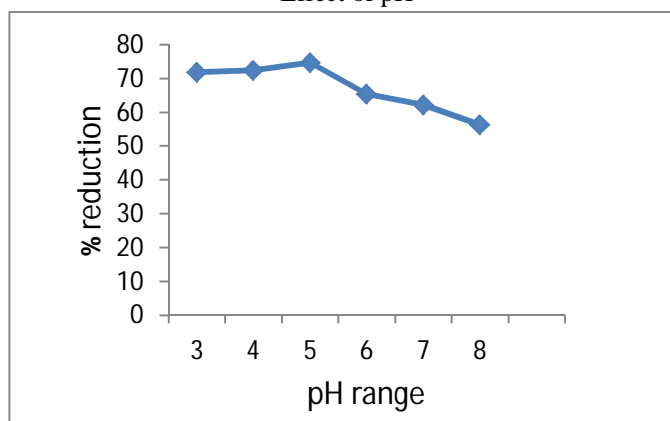
Values of R	Type of Langmuir and Freundlich isotherm
$R > 1$	Unfavorable
$R = 1$	Linear
$0 < R < 1$	Favorable
$R = 0$	Irreversible

The need to apply the Langmuir and Freundlich adsorption isotherms, a series of solutions containing different initial concentrations of Cu ions (5, 10, 15, 20 and 25mg/L) were prepared and employed in the batch adsorption studies at room temperature and optimum conditions obtained previously. They were shaken for 90 minutes with speed 220rpm at room temperature and left still for 24 h. Water samples were filtered and analyzed.

III. RESULT AND DISCUSSION

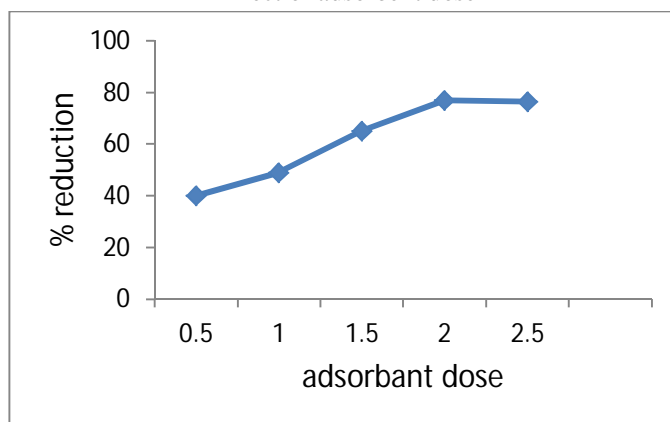
A. Banana peel

Effect of pH

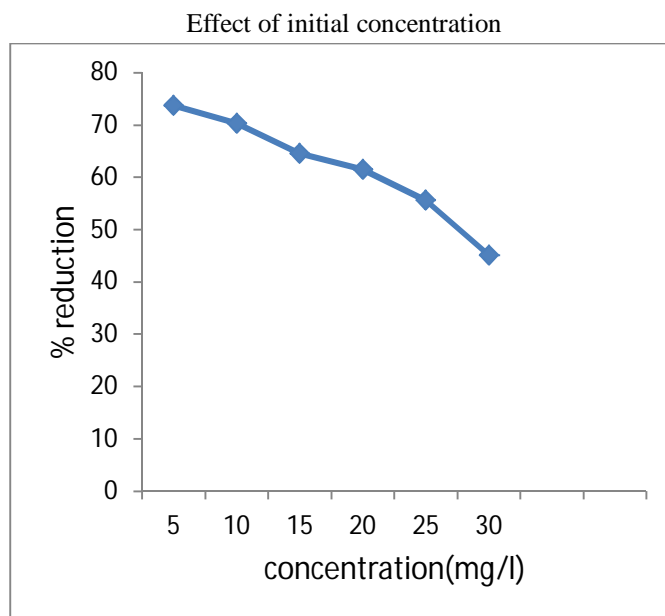


The effect of pH on adsorption was studied by varying the range of pH from 3 to 8. From the graph it has been observed that the adsorption of copper ions is increasing from pH 3 to 5 and afterwards it shows decrease in the adsorption. The maximum adsorption is observed at pH 5 with 74.66 % removal of copper ions.

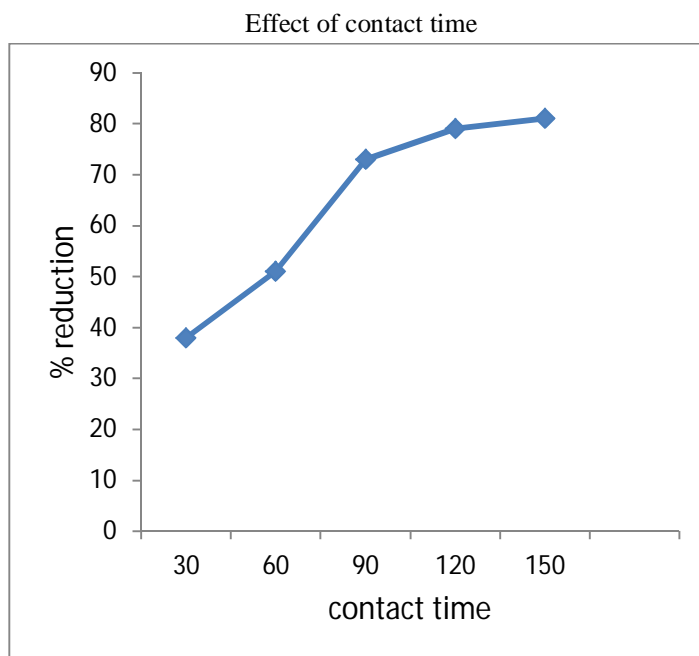
Effect of adsorbent dose



The effect of adsorbent dose on adsorption was studied by varying the dose from 0.5 gm to 2.5 gm. From the graph it has been observed that the adsorption of copper ions is increasing from 0.5 gm to 2.5 gm and afterwards it shows a small decrease in the adsorption. The maximum adsorption is observed at dose of 2 gm with 77% copper removal.

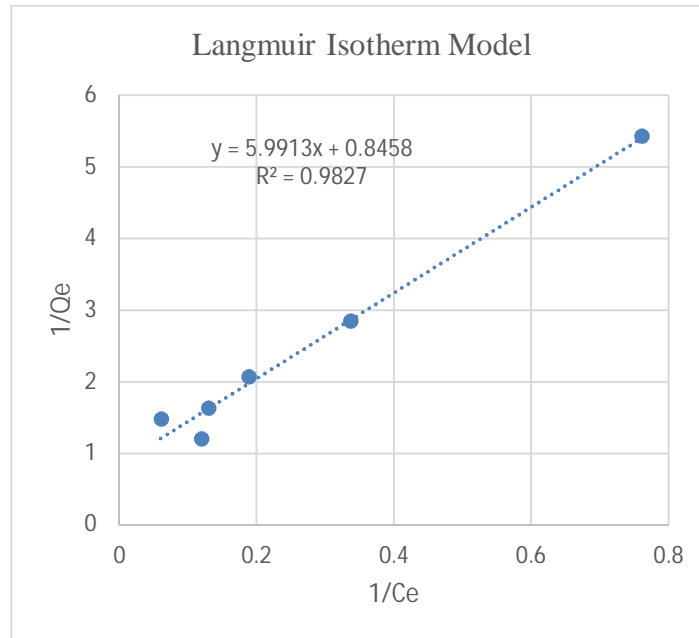


The effect of initial ion concentration on adsorption was studied by varying the concentration from 5 mg/l to 30 mg/l. From the graph it has been observed that the adsorption of copper ions is decreasing from 5 mg/l to 30 mg/l. The maximum adsorption is observed at concentration of 5 mg/l with 73.71% removal.



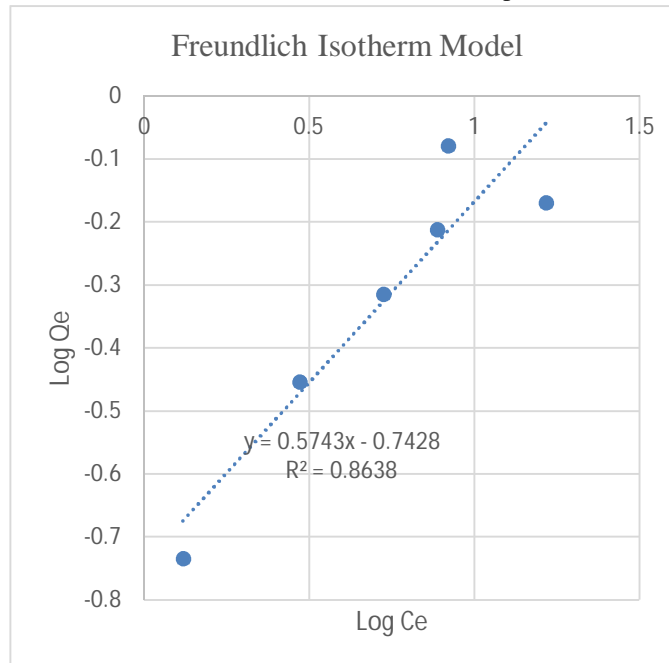
The effect of contact time on adsorption was studied by varying the contact time from 30 minute to 150 minute. From the graph it has been observed that the adsorption of copper ions is increasing from 30 min. to 150 min. The maximum adsorption is observed at 150 minute with 81 % removal of copper ions.

Effect of concentration on Langmuir adsorption isotherm



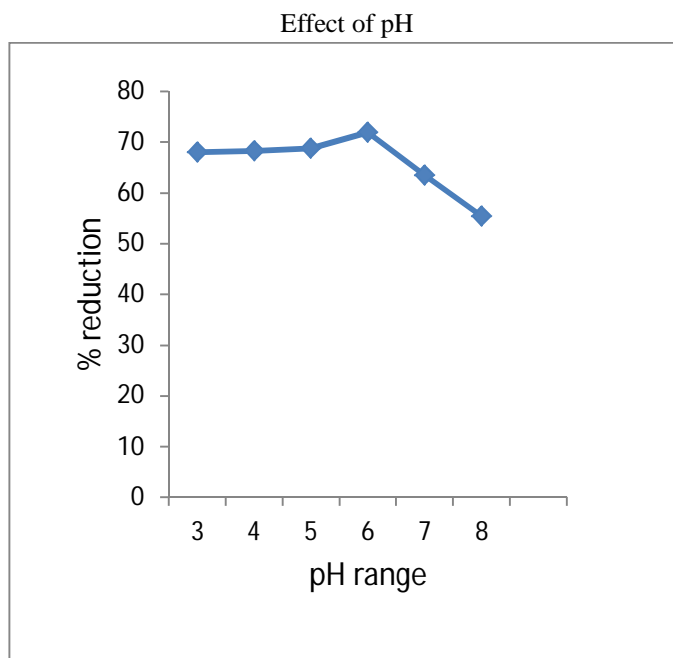
The effect of concentration for the removal copper ions shows that Langmuir isotherm are the best fitting the data than Freundlich isotherm as the value of R^2 is less than on

Effect of concentration on Freundlich adsorption isotherm

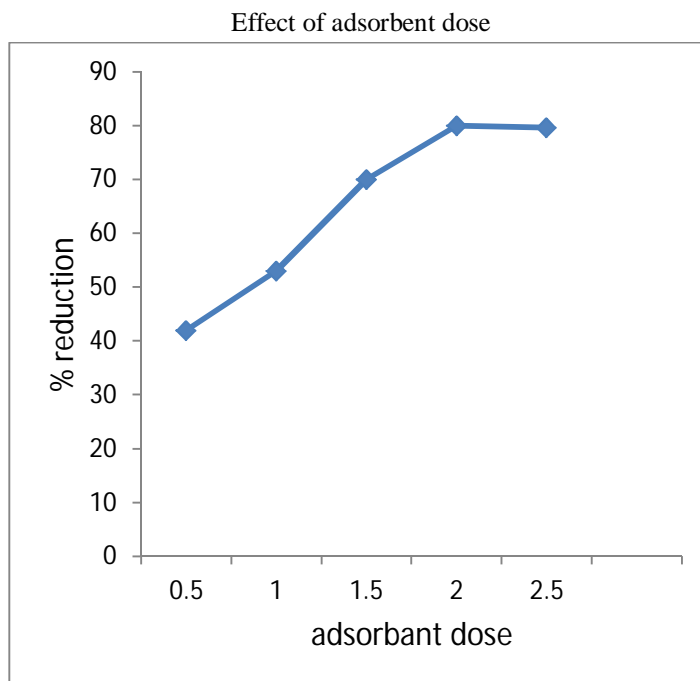


The effect of concentration for the removal of copper ions shows that Freundlich isotherm are fitting the data but less than Langmuir isotherm.

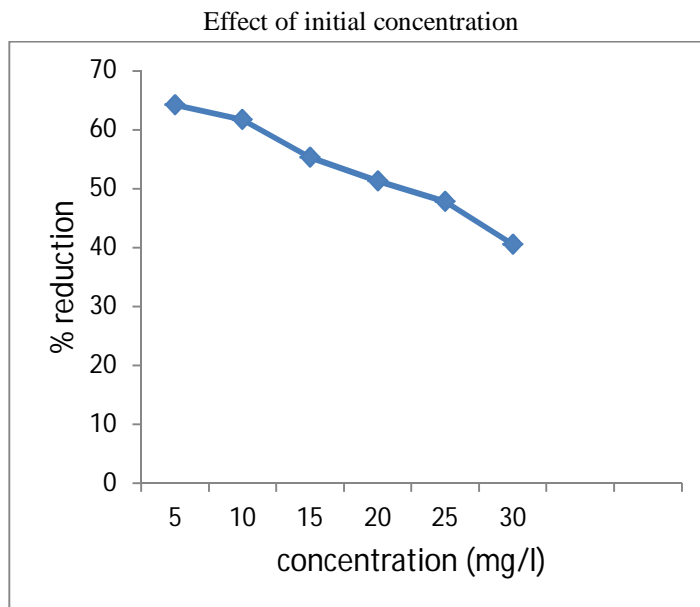
B. Activated Soil



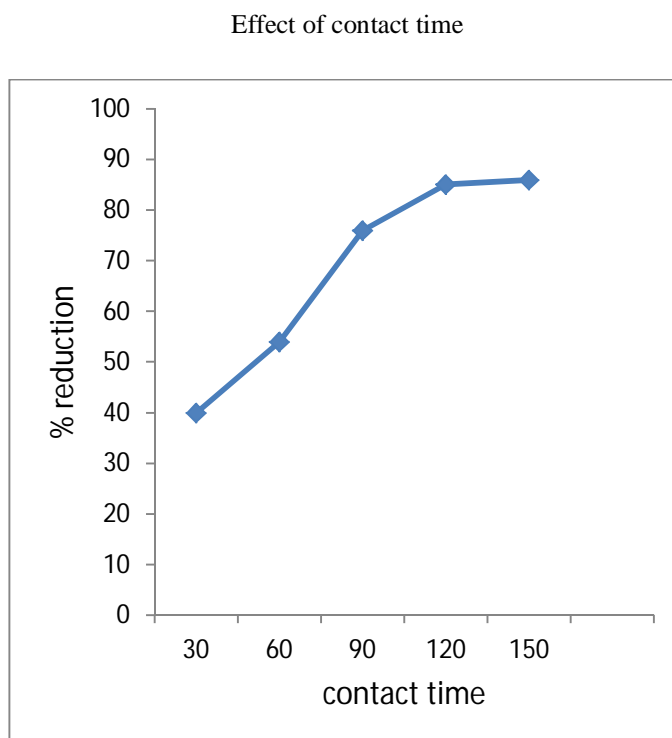
The effect of pH on adsorption was studied by varying the range of pH from 3 to 8. From the graph it has been observed that the adsorption of copper ions is increasing from pH 3 to 5 and afterwards it shows decrease in the adsorption. The maximum adsorption is observed at pH 6 with 72 % removal of copper ions.



The effect of adsorbent dose on adsorption was studied by varying the dose from 0.5 gm to 2.5 gm. From the graph it has been observed that the adsorption of copper ions is increasing from 0.5 gm to 2.5 gm and afterwards it shows a small decrease in the adsorption. The maximum adsorption is observed at dose of 2 gm with 80 % copper removal.

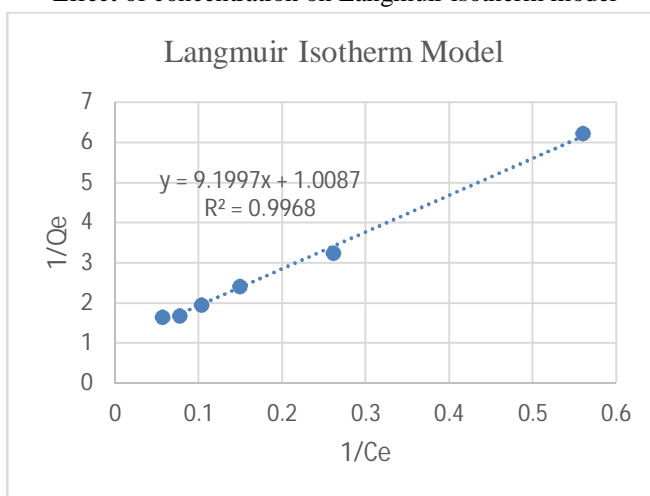


The effect of initial ion concentration on adsorption was studied by varying the concentration from 5 mg/l to 30 mg/l. From the graph it has been observed that the adsorption of copper ions is decreasing from 5 mg/l to 30 mg/l. The maximum adsorption is observed at concentration of 5 mg/l with removal of 64.27 %.



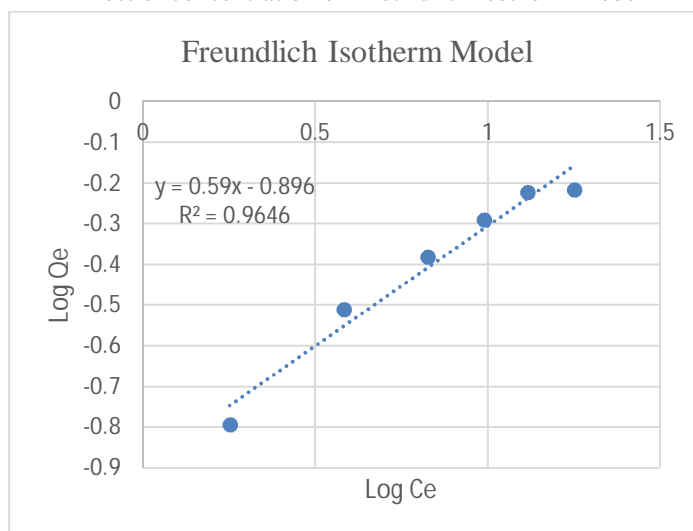
The effect of contact time on adsorption was studied by varying the contact time from 30 minute to 150 minute. From the graph it has been observed that the adsorption of copper ions is increasing from 30 min. to 150 min. The maximum adsorption is observed at 150 minute for activated soil 69.87 % removal.

Effect of concentration on Langmuir isotherm model



The effect of concentration for the removal of copper ions shows that Langmuir isotherm are the best fitting the data.

Effect of concentration on Freundlich isotherm model



The effect of concentration for the removal of copper ions shows that Freundlich isotherm are also best fitting the data.

IV. CONCLUSION

- 1) Banana peels and activated soil are easily available and natural materials for preparing adsorbent. This study has explored the economically viable adsorbents for copper removal from water.
- 2) The pH is an important parameter, which affects the adsorption process. Maximum percentage removal of metal ion is observed at a pH of 5 for banana peels and 6 for activated soil.
- 3) The increase of adsorbent dosage had resulted in the increase of percentage removal, the maximum percentage removal was at 2 g for both banana peels and activated soil.
- 4) The percentage removal increases with increase in contact time which is maximum at 150 minute for both adsorbents.
- 5) The adsorption was decreased with increasing initial metal ions concentration from 5 mg/l to 30 mg/l.

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