

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

Department of Chemical Engineering



B. Tech. Thesis on

**Removal of pollutant from industrial effluent using
ion – exchange resin**

Submitted by

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Under the guidance of

Mrs. Susmita Mishra



CERTIFICATE

This is to certify that the work in this thesis entitled “**Removal of pollutant from industrial effluent using ion – exchange resin**” submitted by **Preeti Agarwal** in partial fulfillments for her requirements for the award of Bachelor of Technology Degree in Chemical Engineering session 2008-12 at National Institute of Technology, Rourkela has been carried out under my supervision and guidance. To the best of my knowledge the matter embodied in the thesis is her bona fide work.

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ABSTRACT

Heavy metals are found as pollutant in industrial waste waters. Mainly it is originating from chemical manufacturing, painting and coating, extractive metallurgy, mining, nuclear, and other industries. Heavy metals exert a deleterious effect on the fauna and flora of lakes and streams. One of the potential remedies to this problem is the use of adsorption technologies. A resin named Tulsion A-23 is used for the removal of copper ion from water in this experiment. Aim of the experiment is to study the influences of various factors, such as contact time, pH of solution, initial adsorbate concentration, initial metal ion concentration and temperature, on the sorption and optimize their values. Experimental results show that resin had a good adsorption capacity for copper and could reduce the concentrations of copper in the wastewater. Suitable time for the operation is found to be 110 min. at solution pH of 6 with 400mg/L of resin and initial concentration of copper 60mg/L. Removal of copper at these optimized parameter is found to be 99.25 %. After that the removal of copper becomes practically very slow. The experimental data is well fitted with Temkin adsorption isotherm and follows second order rate kinetics. Based on these results we can conclude that it is possible to use this resin for removing copper from wastewaters.

CONTENTS

Sl. No	Titles	Page No.
	Certificate	i
	Acknowledgement	ii
	Abstract	iii
	List of Figures	vi
	List of Tables	vi
	Nomenclature	vii
Chapter 1	Introduction	1
Chapter 2	Literature Review	3
2.1	Chemical precipitation	3
2.2	Ion-exchange	4
2.3	Membrane filtration	4
2.4	Electrochemical techniques	5
2.5	Biological methods	5
2.6	Adsorption	6
Chapter 3	. Experimental work	7
3.1	Materials and methods	7
3.1.1	Adsorbent used	7
3.1.2	Chemicals	7
3.1.3	Stock solution preparation	8
3.1.4	Adsorption Experiment procedure	8

Chapter 4	Result and discussion	9
4.1	Effect of various parameters	9
4.1.1	Effect of Contact time	9
4.1.2	Effect of pH	10
4.1.3	Effect of adsorbent dose	11
4.1.4	Effect of initial metal concentration	12
4.1.5	Effect of temperature	13
4.2	Adsorption Isotherms	14
4.2.1	Langmuir isotherm model	14
4.2.2	Freundlich isotherm model	15
4.2.3	Temkin isotherm	16
4.3	Adsorption Kinetics Model	17
4.3.1	Pseudo-first order model	17
4.3.2	Pseudo-second order model	18
Chapter 5	Conclusion	20
5.1	Conclusion	20
5.2	Future scope of the work	20
Chapter 6	References	21

List of Figures:

Fig. No.	Fig. Caption	Page No.
Fig. I	Effect of contact time on copper removal	9
Fig. II	Effect of pH on copper removal from solution	10
Fig. III	Effect of dose of adsorbent on copper removal	11
Fig. IV	Effect of Initial metal concentration on removal of copper	12
Fig V	Effect of temperature on removal of copper	13
Fig VI	Langmuir isotherm for Cu on TULSION A-23 resin	14
Fig. VII	Freundlich adsorption isotherm for Cu on TULSION A-23 resin	15
Fig. VIII	Temkin adsorption isotherm for Cu on TULSION A-23 resin	16
Fig. IX	1st order rate kinetics	18
Fig. X	2nd order rate kinetics	19

List of Tables:

Table I	Characteristic properties of the ion exchange resin used	7
Table II	Freundlich, Langmuir and Temkin isotherms	17
Table III	Rate kinetics model	19

Nomenclature:

US EPA - U.S. Environmental Protection Agency

WHO - World Health Organization

CEPT - Chemically enhanced primary treatment

NF - Nanofiltration

C_0 - Initial metal ion concentration (mg/L)

C_i - Final metal ion concentration in the solution (mg/L)

q - Amount of copper adsorbed (mg/g)

C_e - the equilibrium concentration of copper in solution (mg/L),

Q_o - the amount of adsorbate at complete monolayer coverage (mg/g)

b - Langmuir isotherm constant that relates to the energy of adsorption (L/mg)

K_F, n - Freundlich equilibrium constants

k_1 - rate constant of the pseudo-first-order adsorption (min^{-1})

k_2 - rate constant of the pseudo-second-order adsorption ($\text{g}/(\text{mg min})$)

CHAPTER -1

INTRODUCTION

Industrial effluent is the waste water generated by some industrial activity. Many industries have a need to treat this water to obtain very high quality water for many demanding purposes. Ion exchange using natural or synthetic resins removes metals like calcium, copper, magnesium, cadmium etc. from water, replacing them with hydrogen and hydroxyl ions. Regeneration of ion exchange columns with strong acids and alkalis gives a wastewater rich in hardness ions which are readily precipitated out, especially when in a mixture with other wastewaters. Mostly water is purified for human consumption but water purification may also be designed for a variety of other purposes, including the requirements of medical, pharmacology, chemical and various industrial applications.

Copper is an important engineering material with wide industrial application and is an essential factor for animal metabolism. Extensive intake of Cu in human body causes hemolysis, hepatotoxic and nephrotoxic effects like vomiting, cramps, convulsions, or even death. The maximum contaminant level for copper in surface water must be 1.3 mg/L (USEPA).

Copper enters into the environment through sources such as natural and anthropogenic. The contamination of air and water, by copper is contributed from the following sources:

- Mining and metallurgy industries.
- Electroplating industries.
- Refining copper ores.
- Milling.
- Petroleum and refining.
- Chloro-alkali industries.
- Explosives.
- Battery manufacturing.
- Copper –ammonium rayon industries and brass industries[1,2].

Copper is also discharged into the environment by natural sources like windblown dust, decaying vegetation, volcanic emissions, forest fire and sea sprays[3].

Copper is a metal of choice for technologists and is an important engineering material having a wide range of industrial applications.

- An important use of copper is in alloys such as brass, bronze, gunmetal, Monel metal and German silver.
- In ceramics and pesticides.
- Used in manufacture of wires for various industries, namely electrical, electronics, automotive, electrical appliances, white goods, etc.
- In copper forming industries .
- Copper tubing is used in plumbing.
- Used in electroplating.
- Copper is sometimes combined with nickel to make a corrosion resistant material that is used in shipbuilding.[4,5].

Apart from industrial use copper plays an important role in all organisms, including man. Copper can be used as a pesticide as well as a nutrient. Copper is an essential nutrient with daily dietary amounts of 1-2 mg requirement for adults. It is a natural anti plaque and anti bacterial agent. It is a component of hemocyanin, the blue, oxygen-carrying blood pigment of lobsters and other large crustaceans. Copper is needed for certain critical enzymes to function in the body.

Some harmful effects are also associated with use of copper. Copper is one of the toxic heavy metals, which 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. Moreover, continued inhalation of copper containing sprays is linked to an increase in lung cancer among exposed workers. Excessive intake of copper causes harmful biochemical effects, and it may cause hemolysis, hepatotoxic and nephro toxic effects in human beings. Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea. Copper toxicity leads to serve muscosal irritation, corrosion, widespread capillary damage, hepatic and renal damage and nervous system irritation followed by depression.

So the removal of copper is very necessary. It should be within the intake limit so as to have no harm to environment[6,7].

CHAPTER -2

LITERATURE REVIEW

According to the WHO standards the maximum contamination level of copper is 1.3 mg L^{-1} . The majority of the industries are discharging effluents containing copper more than its permissible limit. Thus the removal of copper from the industrial wastewater before releasing is necessary. There are several convectional techniques available for the removal of copper ions from wastewaters[8,9,10].

- Chemical precipitation.
- Ion -exchange.
- Membrane filtration.
- Electrochemical methods.
- Biological methods.
- Adsorption methods.

2.1 Chemical precipitation:

Pauline[11] reported the removal efficiencies of copper from raw wastewater by chemically enhanced primary treatment (CEPT). The removal was found to be 79%. They found that the Enhanced coagulation and flocculation by ferric chloride and anionic polymer can increase the dissolved metal removal efficiencies. Chen et al[12] investigated the removal of copper using precipitation process by lime precipitant. The percentage removal achieved was 99.37%- 99.6% at pH 7-11 respectively.

Ngatenah et al[13] employed precipitation to remove copper from aqueous solution using Groundwater Treatment Plant Sludge (GWTPS). The optimum conditions for 100% removal were found to be pH between pH 2 and pH 2.5, contact time varied from 90 min to 480 min.

2.2 Ion-exchange:

Erol and Turkan[14] investigated the removal of copper from aqueous solution by ion - exchange process using Lewatit CNP 80 resin (weakly acidic) and Lewatit TP 207 (weakly acidic and chelating). They found the optimum pH range for the ion-exchange of copper on Lewatit CNP 80 and Lewatit TP 207 were 7.0–9.0 and 4.5–5.5, respectively. Selvaraj et al[15] employed ion-exchange process to treat copper containing waste water by Amberjet 1500H and Ambersep 252H resins. From the adsorption isotherm studies they observed that the uptake capacity of Cu (II) on 1500H is larger than that of 252H due to the intrinsic ion exchange capacity, while the adsorbate interaction of 1500H is smaller than that of 252H.

Liu and Erhan[16] used ion-exchange process to remove copper from aqueous solution by Carboxylate-Containing Resin. The maximum adsorption capacity of copper obtained on the resin at pH5.0 was found to be 192 mg/g. Doula[17] employed clinoptilolite - Fe system to remove Cu, from drinking water. He found that the system has very large metal adsorption capacity and for most of the cases the treated water samples were suitable for human consumption or agricultural use.

2.3 Membrane filtration :

Camarilloa et al[18] employed ultrafiltration technique by polymer enhanced ultrafiltration ceramic membrane to treat copper from wastewater. Yang and Kocherginsky investigated the use of hollow fibre supported liquid membrane (HFSLM) system to remove copper from ammonical waste water. Based on the empirical correlations they estimated that the overall mass transfer resistance through HFSLM is higher than total of the element resistances in the tube side, shell side and the membrane. Tanninen et al[19] studied removal of copper from waste water using Nanofiltration process at 0.47 M initial metal concentration. They found the maximum removal up to 96%-98% at 20 bar. Hani and Hassan[20] employed Reverse osmosis and Nanofiltration(NF) technique to remove copper from aqueous solution. From the results they found that high removal efficiency of the heavy metals could be achieved by RO process (98%). Through NF, up to 90% of the copper ions were removed.

2.4 Electrochemical techniques :

Escobar et al[21] investigated electro-coagulation process to remove copper from natural waters and wastewater using electrodes of commercial laminate steel. They identified the optimum conditions for the process as pH 7, flow rate $6.3 \text{ cm}^3/\text{min}$ and a current density between 31 A/m^2 and 54 A/m^2 and when the electrode geometric area and time of electrolysis reached critical values, the copper removal reached a maximum value of 80%.

Akbal and Camcı[22] reported the removal of copper from metal plating industry using Fe- Al electrodes. They found from the results that electrocoagulation with a Fe–Al electrode pair efficiently removed 100% Cu, at an electrocoagulation time of 20min, a current density of 10 mA/cm^2 and at pH 3.0. Khelifa et al[23] found the optimum conditions for the maximum Cu removal (99%) was pH 6 and current density 0.3A. Chang et al[24] used electrodeposition process in conjunction with ultrasound to remove copper from wastewater. They found that the technique can successfully remove copper (95.6%) from wastewater.

2.5 Biological methods:

Gupta et al[25] investigated biosorption of copper aqueous solutions by green alga *Spirogyra* species. They observed the maximum biosorption capacity of $133.3 \text{ mg Cu (II)/g}$ of dry weight of biomass at an optimum pH of 5 in 120 min with an algal dose of 20 g/L . Hossain and Anantharaman[26] employed biosorption of copper by *Thiobacillus ferrooxidans*. They found the maximum biosorption of copper to be 94.25% within 60 hr of inoculation time with optimum pH 4.5 and temperature 40°C for 700ppm initial copper loading. Narsi et al[27] used the dead biomass of *spirogyra* species, for the removal of copper from aqueous solution. It was observed that the *spirogyra* species shown much better sorption in the pH between 6-7 and at contact time of 30 min. The maximum uptake found was 34.94 mg/g .

2.6 Adsorption:

Gaikwad[28] employed adsorption process to remove copper from wastewater using activated carbon derived from coconut shell. From the results he found that the adsorption follows first order kinetics and is slightly endothermic. Yao et al[29] employed batch adsorption studies to remove copper from aqueous solution by chestnut shell. They observed that there was a sharp increase in the copper removal from 20.4% to 92.4% occurred when the pH values of the solutions changed from 2.0 to 5.0. Jaman et al[30] used rice husk as a low cost adsorbent for the removal of copper from wastewater. From the experimental results they observed that almost 90–98% of the copper could be removed using treated rice husk. They found the results that the adsorption equilibrium data fitted the Langmuir adsorption model very well at different temperatures. Tariq et al[31] employed adsorption of copper from aqueous solution on to pine fruit a solid adsorbent. From the results they found that the adsorption was pH dependent. The optimum pH for the removal Cu^{+2} was 7.0, the highest adsorption capacity was found to be 14.1 mg of metal ion per gram of adsorbent at initial concentration of 57.6 mg/L of copper ions. The percentage removal was found to be 94.1-96% along the whole range of initial concentrations.

Apart from batch studies, adsorption process are also carried out in in different continuous column, which helped in scaling up the laboratory data to pilot or industrial scale. In these process applications, a packed bed column is an effective process for cyclic sorption/desorption, as it makes the most tremendous use of the concentration difference known to be a driving force for heavy metal sorption and results in a improved quality of the effluent.

CHAPTER - 3

EXPERIMENTAL WORK

3.1 MATERIALS AND METHODS:

3.1.1 Adsorbent used

The anion exchange resin Tulsion A-23, (THERMAX LIMITED CHEMICAL DIVISION Pune) used in the study for the removal of heavy metals from water and waste water. Their physical properties and specification are presented in Table 1[32].

Table I: characteristics properties of the ion exchange resin used

Type	Strong Base Anion Exchange Resin
Matrix structure	Cross-linked polystyrene
Physical form	Moist spherical beads
Ionic form as supplied	Chloride
Moisture holding capacity	53 + 3%
Particle Size	0.3 to 1.2 mm
pH range	0 to 14
solubility	insoluble in all common solvents

3.1.2 Chemicals:

All the chemicals used were of analytical reagent grade. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is used for preparation of copper stock solution. Hydrochloric acid and Sodium hydroxide were used to adjust the solution pH. Distilled water is used throughout the experimental studies.

3.1.3 Stock solution preparation:

A stock solution of Cu^{+2} (1000 mg L^{-1}) was prepared by dissolving 3.929 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 1000 ml distilled water.

Procedure:

A standard solution of concentration 10 mg/L of copper was prepared. For this 9.82 mg of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was added in 250 ml of distilled water. Then 200 ml of this solution was pipetted out into 500 ml volumetric flask. The pH of the solution is checked using pH meter and it is found to be 7.16. To make the concentration of resin 600 mg/L, 120 mg resin is added to solution. The concentration of copper is analyzed by collecting sample after every 10 min. till 2 hours.

3.1.4 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 atomic absorption spectrophotometer for the remaining copper ion concentration. Experiments were carried out at initial pH value 7.15. The percent removal of metals from the solution was calculated by the following equation.

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

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

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

CHAPTER - 4

RESULT AND DISCUSSION

4.1 STUDY OF EFFECT OF VARIOUS PARAMETERS:

4.1.1 Effect of Contact time:

The removal of copper from aqueous solution was studied as function of contact time in the range of 0-120 min at 10mg/L initial metal concentration, 7.16 pH, 600mg/L resin, and 25°C temperature. The effect of contact time on removal of copper is shown in the Fig I. From the figure it was observed that the rate of copper removal was higher at the beginning until 50min and, thereafter, the adsorption rate become practically very slow and after 110 min. it starts decreasing. The difference in the degree of adsorption may be due to the fact that in the beginning all the sites on the surface of the adsorbent were vacant and the solute concentration gradient was relatively high. As a result, the extent of copper removal decreased with increase in contact time, which is dependent on the number of vacant sites on the surface of resin. Based on these results 110min was considered as the optimum time for the rest of the experiments[33].

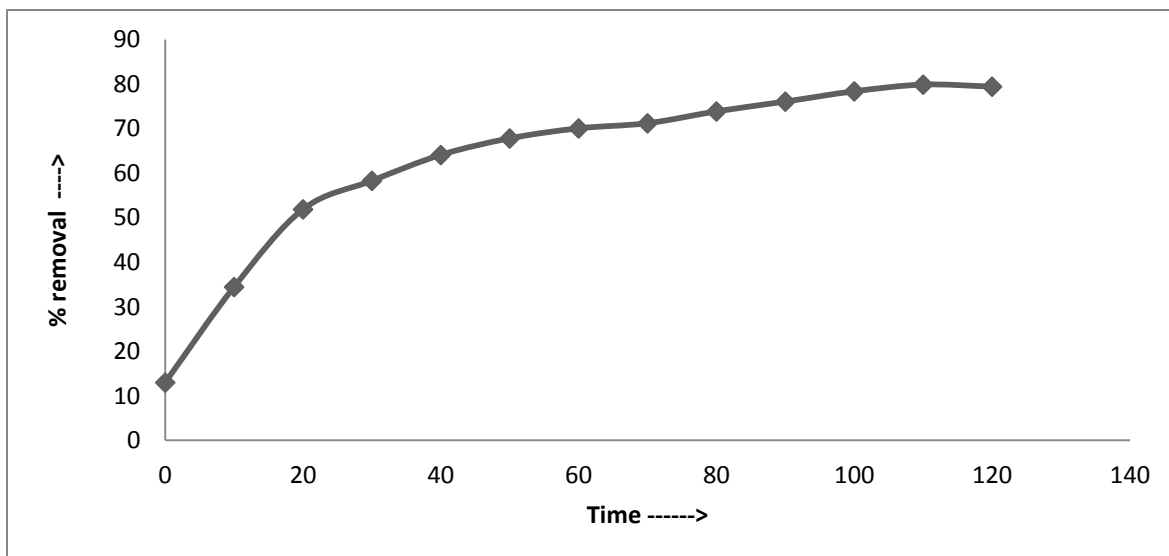


Fig. I: Effect of contact time on copper removal.

4.1.2 Effect of pH:

The pH of solution has significant impact on the uptake of metals, since it determines the surface charge of the adsorbent, the degree of ionization and specification of the adsorbate. The variation of pH affects the effectiveness as hydrogen ion itself is a tough competing adsorbate[34].

The effect of pH on adsorption of copper is shown in Fig. II. The effect of pH on adsorption of copper was studied at 25°C, initial metal concentration 10mg/L, adsorbent dose 0.6g/L by varying the pH of metal solution from 2-12. The percentage adsorption increases with increase in pH. 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 favoured adsorption compared to M (II) 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 [35]. Further increase in pH i.e., above 7 of the solution causes precipitation of copper ions on the surface of the adsorbent by nucleation. From these results it was clear that at pH 6 the metal uptake was more i.e.,96.30%, so pH 6 was taken as optimum pH for rest of the experiments.

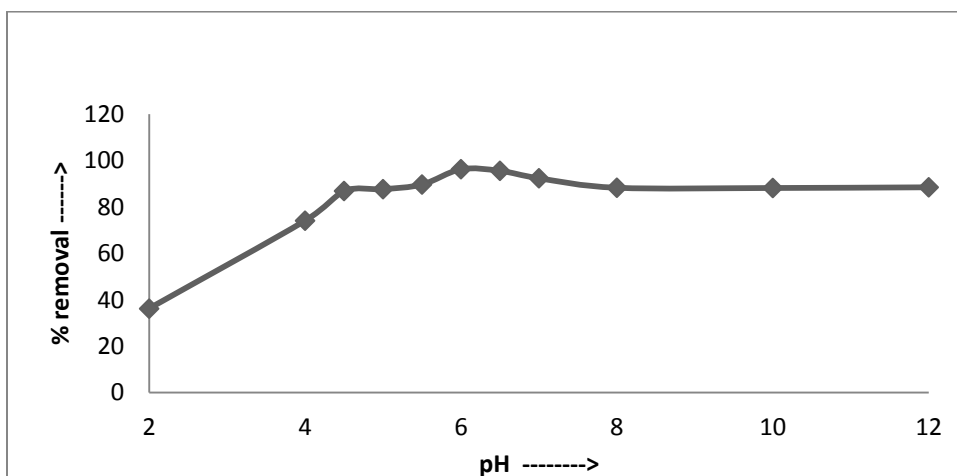


Fig. II Effect of pH on copper removal from solution.

4.1.3 Effect of adsorbent dose :

Effect of resin on copper adsorption was studied at 10mg/L, 25°C, and pH 6. The results of adsorbent dose on the percentage removal of Copper on resin is reflected in Fig III. Initially the metal uptake increased with adsorbent dose 0.2g/L to 0.4g/L and then started decreasing continuously. It is due to increased adsorbent surface area and availability of more adsorption sites. But at 0.4g/L adsorbent dose the metal ions adsorbed per unit weight of adsorbent decreased which is due to the fact that at higher adsorbent dose the solution ion concentration drops to a lower value of q (amount adsorbed) indicating the adsorption sites to remain unsaturated [36]. Based on these results 0.4g/L was taken as optimum adsorbent dose for the rest experiments.

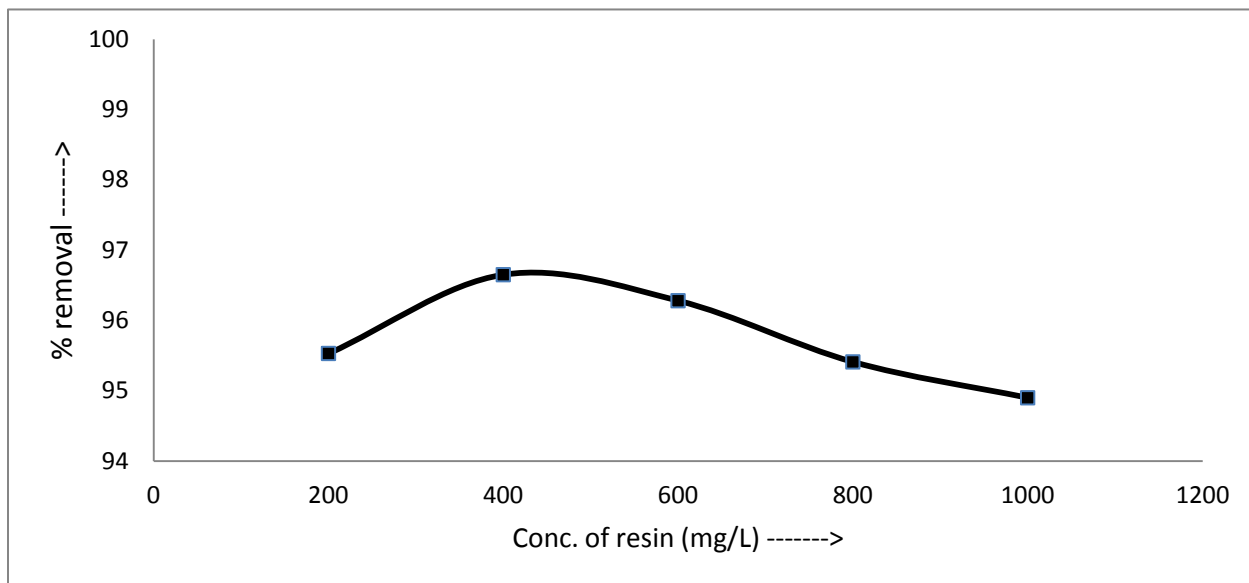


Fig. III Effect of dose of adsorbent on copper removal

4.1.4 Effect of initial metal concentration :

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 (10 to 70 mg/L) by resin (0.4g/L) at 110 min contact time and at pH 6 has been depicted in the Fig.IV. The percentage copper adsorbed increased 96.65% to 99.3% with increase in initial concentration from 10mg/L to 70mg/L. More adsorption at higher initial metal concentration may be responsible for increasing percentage removal at increasing initial metal concentration. It reflects that the resistance to mass transfer reduces therefore the removal decreases at higher metal concentration. Similar results were reported by other researchers [37]. Based on the experimental values, 60mg/L Copper concentration is selected as the optimized value for further use.

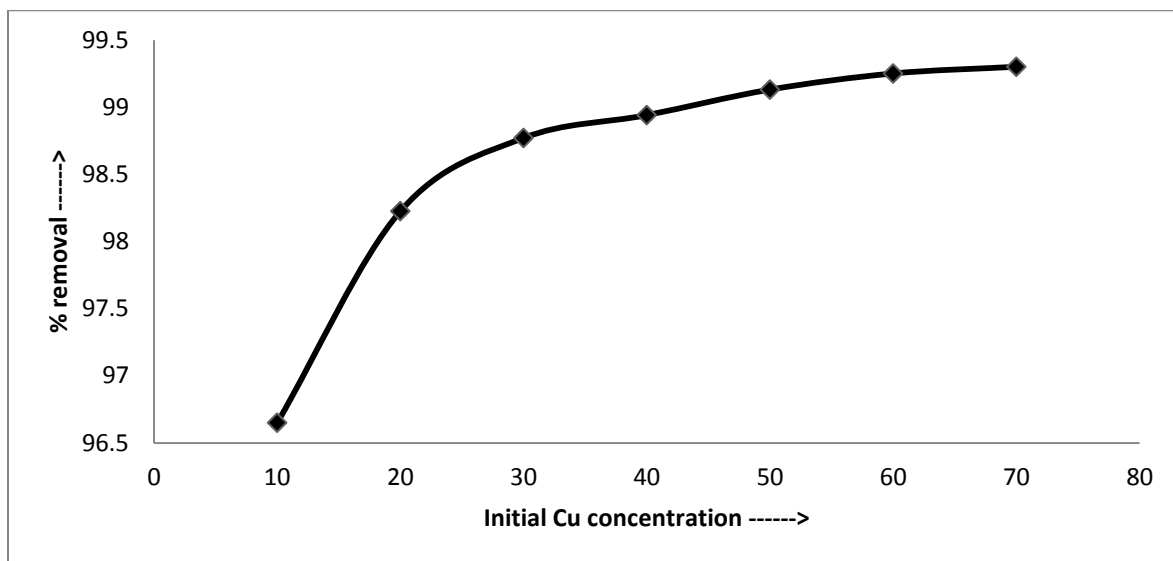


Fig. IV. Effect of Initial metal concentration on removal of copper

4.1.5 Effect of temperature:

The effect of temperature for the adsorption of copper metal ions onto resin was studied. It is found that the % removal of copper remains almost constant for the temperature range of 25°C to 40°C. There is a very little decrease in concentration of copper at very high temperature. This may be due to the endothermic adsorption of divalent cations[38].

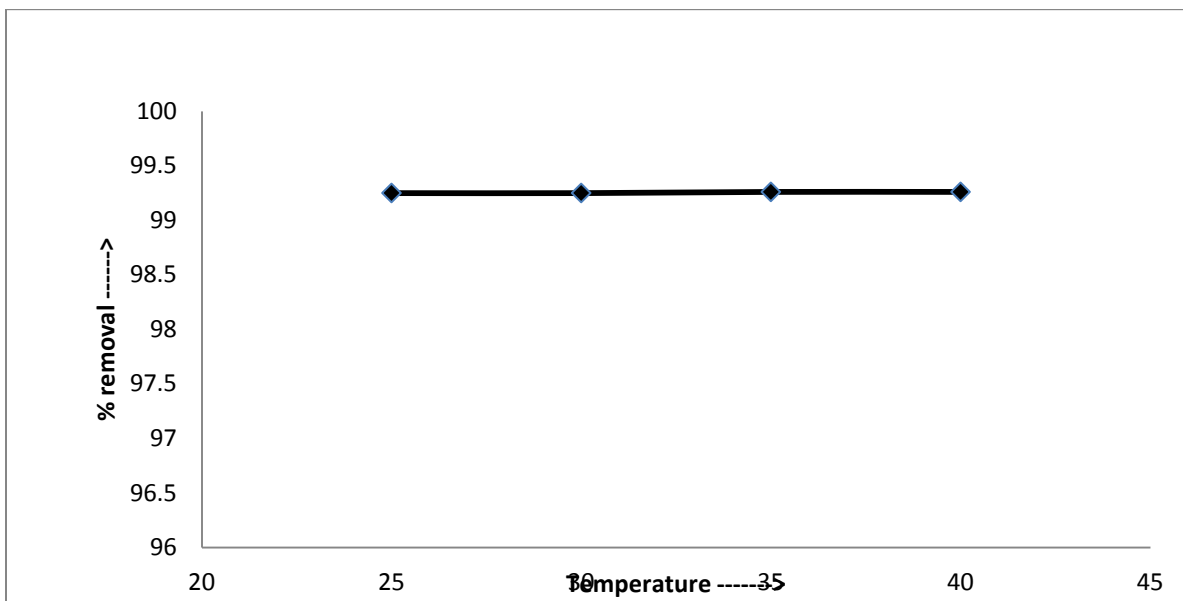


Fig V. Effect of temperature on removal of copper

4.2 ADSORPTION ISOTHERMS:

To quantify the adsorption capacity of TULSION A-23 resin for copper adsorption, two-parameter equations namely Freundlich, Langmuir and Temkin isotherms have been adopted. Adsorption isotherm and kinetic studies were carried out with different initial concentrations of copper while maintaining the resin dosage at a constant level.

The study of the adsorption equilibrium was carried out for metal concentrations varying from 10 to 70mgL⁻¹. The obtained experimental data here are expectedly well fitted with the linearized form of Langmuir, Freundlich and Temkin models.

4.2.1 Langmuir isotherm model:

The Langmuir isotherm is perhaps the best known of all isotherms describing adsorption and its linear form is represented by,

$$\frac{1}{q_e} = \frac{1}{Q_o} \frac{1}{b C_e} + \frac{1}{Q_o} \quad (2)$$

Where,

q_e = the amount of copper adsorbed per unit weight of the adsorbent (mg/g),

C_e = the equilibrium concentration of copper in solution (mg/L),

Q_o = the amount of adsorbate at complete monolayer coverage (mg/g)

b = Langmuir isotherm constant that relates to the energy of adsorption(L/mg) [39].

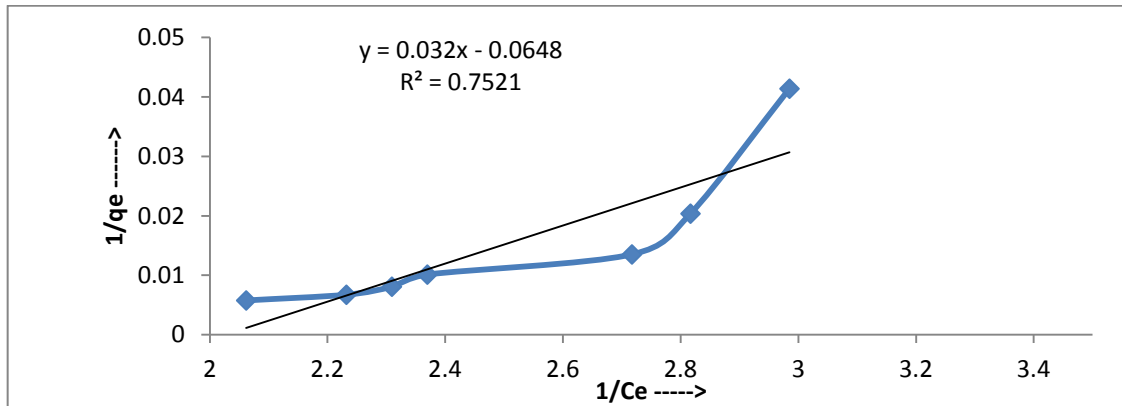


Fig. VI Langmuir isotherm for Cu on TULSION A-23 resin

4.2.2 Freundlich isotherm model:

Freundlich equation is derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces. The Freundlich equation is given by :

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

The logarithmic form of equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

Where,

q_e = amount of metal ion adsorbed per specific amount of adsorbent (mg/g),

C_e = equilibrium concentration (mg/l),

K_F, n = freundlich equilibrium constants[40].

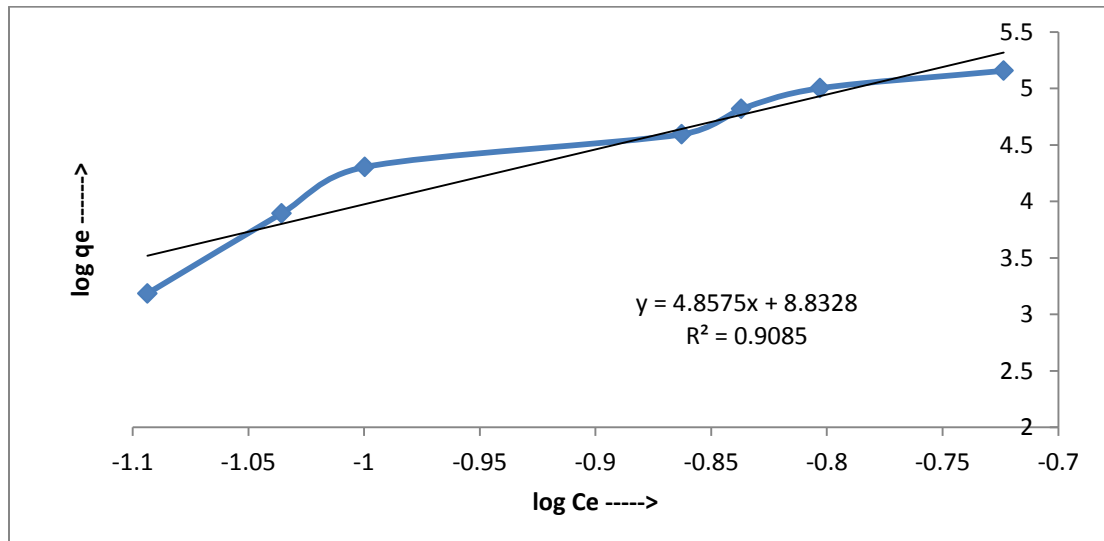


Fig. VII Freundlich adsorption isotherm for Cu on TULSION A-23 resin

4.2.3 Temkin isotherm:

Temkin isotherm assumes that decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies[41]. Temkin isotherm is given by the following equation :

$$q_e = \frac{RT}{b} \ln(aC_e) \quad (5)$$

Linear form of Temkin isotherm is given by the following equation:

$$q_e = a + b \ln C_e \quad (6)$$

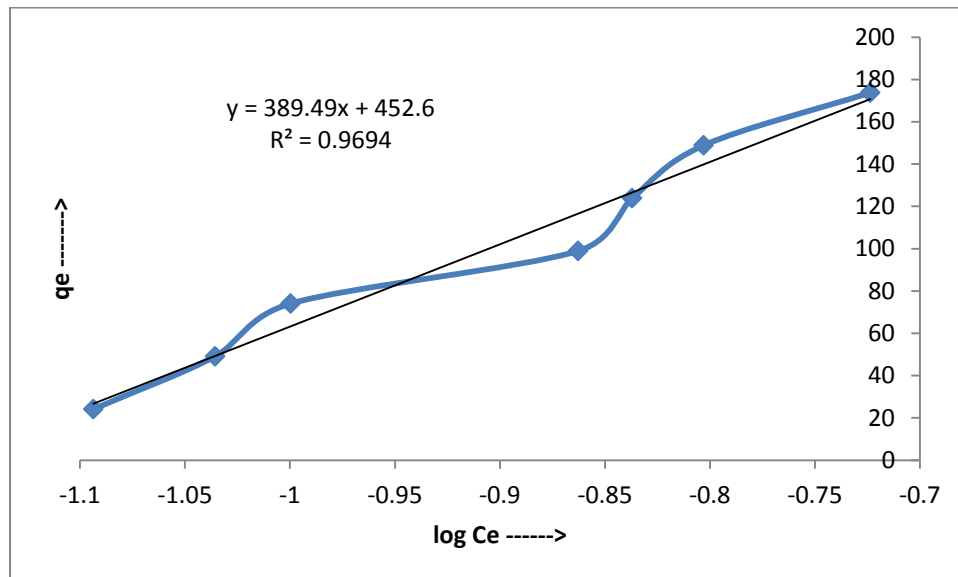


Fig. VIII Temkin adsorption isotherm for Cu on TULSION A-23 resin

Table II : Langmuir, Freundlich and Temkin isotherms :

Temperature(K)	Langmuir			Freundlich			Temkin		
	Q_o	b	R^2	n	$\ln k_f$	R^2	a	b	R^2
298	-15.43	-2.02	0.7521	0.206	8.8328	0.9085	452.6	389.49	0.9694

4.3. ADSORPTION KINETICS MODEL:

The adsorption kinetic model of copper on the adsorbent studied was analyzed by using two kinetic models: pseudo-first order and pseudo-second order models.

4.3.1. Pseudo-first order model:

The model of the pseudo-first order used is that of Lagergren given by the following equation:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (7)$$

Where k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption, q_t (mg/g) denotes the amount of adsorption at time t (min) and q_e (mg/g) is the amount of adsorption at equilibrium[42].

After definite integration by application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, above Eq. becomes.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t \quad (8)$$

The adsorption rate constant, k_1 , can be calculated by plotting $\log(q_e - q_t)$ versus t .

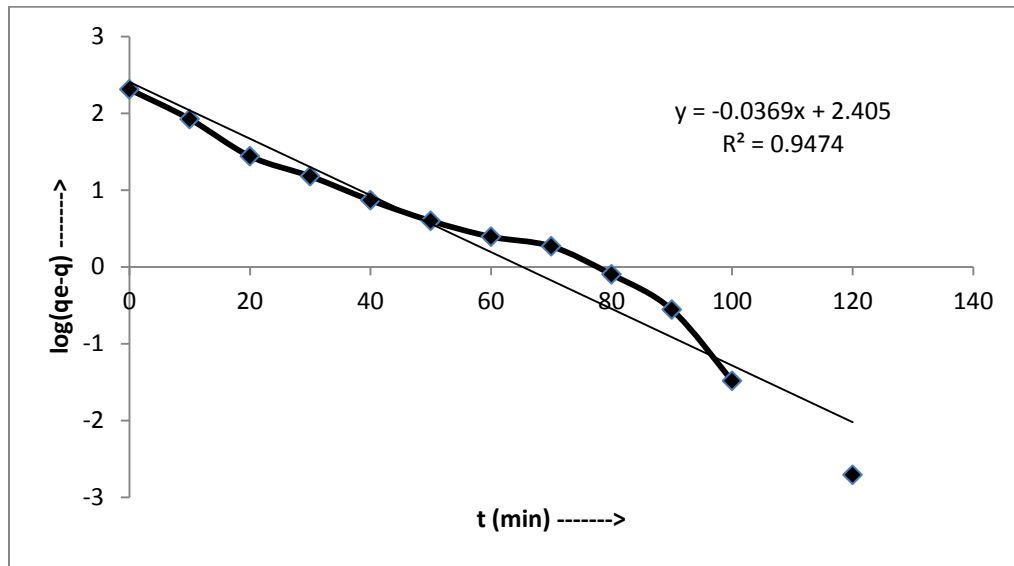


Fig. IX. 1st order rate kinetics

4.3.2. Pseudo-second order model:

The pseudo-second-order equation can be written as :

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

Integration of Eq. and application of the conditions $q_t=0$ at $t=0$ and $q_t = q_t$ at $t = t$,

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \quad (10)$$

Where k_2 (g/ (mg min)) is the rate constant, k_2 and q_e can be obtained from the intercept and slope[42].

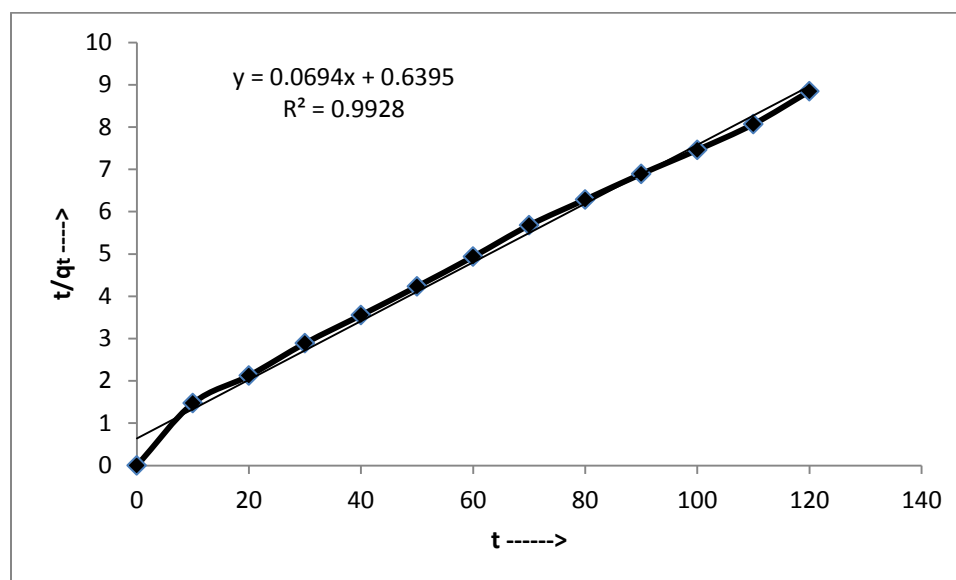


Fig. X. 2nd order rate kinetics

Table III : Rate kinetics model :

1 st order kinetics		2 nd order kinetics	
K_1	R^2	K_2	R^2
0.085	0.9474	0.0075	0.9928

CHAPTER - 5

CONCLUSION

5.1 Conclusion :

In this study, the effects of parameters such as amount of resin, resin contact time, pH, and temperature on ion exchange separation have been investigated.

The following conclusions were drawn based on investigation of copper removal by TULSION A-23 anion exchange resins that the resin is capable of removing copper from aqueous solution to the extent of 99.25% at the solution pH of 6.0. The minimum resin dose required for effective removal was found to be 400 mg/l at pH 6.0 and initial copper ion concentration of 60 mg/L. The contact time in batch process was about 110 min at 25°C temperature and 120 rpm but the resin works even for very low Cu concentration at drinking water pH. The adsorption process obeys the Temkin adsorption isotherm very closely. No desorption was reported upto 110 min indicates that the adsorbed copper remains almost stable on the resins. The results also demonstrate that the process follows second order rate kinetics with rate constant of 0.0075.

5.2 Future scope of the work :

According to the results obtained for the removal of copper, the resin named TULSION A-23 can be used for the removal of other metals also like zinc, cadmium, chromium etc. Experiments can be performed for these metals also to see how much effective this resin is for the removal of other metals. The regeneration studies can also be done for the resin so that it can be used again and again giving higher efficiency in comparison to single cycle.

CHAPTER - 6

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