

# Kinetics and Equilibrium Studies of Cu(II) Ions Adsorption from Aqueous Solutions and Kalpani River on TP260H, SK112H and DMSCH

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## Abstract

Cu<sup>2+</sup> adsorption on the Amberlite Lewatit MDS TP260 (TP260H), DIAION™ SK112 (SK112H), DOWEX™ MARATHON™ MSC (DMSCH) were studied in a batch mode, as a function of pH (3-9), agitation time and different initial concentration ranges (25-120 mg/L and 160-240 mg/L) were studied at a constant temperature of 20°C. The sorption of Cu<sup>2+</sup> increases with the increase in concentration and pH of the solution. However, the Cu<sup>2+</sup> sorption decreases when pH>5 which may not only due to the decrease in the active surface sites because of the formation of Cu(OH)<sub>2</sub> but also due to the surface alteration. The data is found to fit both the Freundlich, Dubinin-Radushkevich and Langmuir equations. Cu<sup>2+</sup> adsorption followed the pseudo-second order kinetics for all the resins. The Freundlich, Dubinin-Radushkevich and Langmuir constants, calculated from the sorption of Cu<sup>2+</sup> on resins were presented and demonstrated the practical utility in the removal of the Cu<sup>2+</sup> ions from water, synthetic wastewater and river of kalpani. In water Cu<sup>2+</sup> was highest followed by Cd and Ni while Cr, Pb and Zn were not detected in water. Whereas the heavy metal accumulation in sediments was in the order of Cu>Zn>Cr>Ni>Pb>Cd. Cu<sup>2+</sup> ions. Sediments and water did not exceed WHO guidelines. Resins used to remove Cu<sup>2+</sup> ions may remove other heavy metals as well. Sorption of Cu<sup>2+</sup> ions in these resins and intraparticle diffusion was the key rate limiting step.

**Keywords:** Copper; Resin; Reaction kinetics; Freundlich isotherm; Langmuir isotherm

## Introduction

Environmental contamination with heavy metal ions has been given a very special attention due to their high toxicity [1,2] and adverse effects. These heavy metal ions tend to accumulate in living organisms, causing various complications when it exceeds specific limits [3,4]. Copper, yet another pervasive pollutant in the environment is a consequent of the continual increase in urbanization and industrial activities. It is very hazardous and elevated concentrations lead to liver damage, hemorrhage, the breakdown of RBCs, mucosal irritation, insomnia and severe hepatic, renal as well as central nervous damage [5-7].

With the recent increased demand for adequate heavy metal removal from water supplies and their specifications in natural aquatic systems have come into focus as a debilitating problem. Different techniques are used to remove toxic copper from waste water through reverse osmosis, chemical precipitation, and adsorption through activated carbon [7-10]. One of the methods that could be used to remove heavy metals from wastewaters is the ion exchange. Many types of research have been carried out in recent years upon ion exchangers and hot great importance in the heavy metal removal from wastewater [3,4]. They are composed of framework which is held together by chemical bonds or lattice energy. The framework possesses positive or negative charges which are compensated by ions of opposite sign, called counterions. Thus depending upon the nature of the counterions bound to the framework, the ion exchangers are subdivided into a) cation exchanger, if the mobile ion of the exchanger is cation and b) anion exchanger, if the mobile ion of the exchanger is anion. However, there are certain materials that are capable of exchanging both cations and anions, called c) amphoteric ion exchangers. Most of our knowledge about ion exchange is derived from numerous investigations that have been made to study thermodynamics, selectivities, and rates of simple cation exchange processes. However, comparatively very little data is available about the sorption of cations on strong cation exchangers [7,11,12].

In numerous studies [13-15], generally, most of the attention is paid to the sorption of Cr<sup>3+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> and Ni<sup>2+</sup> by ion exchange resins. However, the data regarding the cation exchange sorption of Sb<sup>3+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Cu<sup>2+</sup> is very scarce in the literature [16-18]. An attempt was made during the present investigation to quantify and analyze concentrations of heavy metals in water and sediments of Kalpani stream and to study the sorption of Cu<sup>2+</sup> by commercially available strongly acidic cation exchangers, under different experimental conditions of concentration and pH. Kalpani Stream is considered as the life line of part of Mardan and Nowshera districts, flowing from North to South with the length of about 110 km. These resins were selected for the present study because they are cost effective for waste streams Cu<sup>2+</sup> removal (at lower concentrations) as well as their operation over a wide range of pH (0-14) and a high temperature of 120-121°C. Amberlite resins: TP260H, SK112H, and DMSCH are widely used in various practices such as mixed-bed operations, heavy metal adsorption and for nutrient recovery. In electronic process waste water, Cu<sup>2+</sup> ions are present. In our study, a number of well-known adsorption isotherm equations and kinetic parameters as well as the effect of pH, contact time, initial Cu<sup>2+</sup> concentration were studied to describe the Cu<sup>2+</sup> sorption.

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## Nomenclature

- C: Total ion concentration in solution  
 $C_0$ : Initial heavy metal concentration  
 $C_e$ : Equilibrium concentration of solution  
D: Distribution coefficient  
m: Amount of the resin  
K: Freundlich isotherm constant  
k: Equilibrium constant of Langmuir isotherm  
k1: Rate constant of pseudo-first-order adsorption kinetics  
k2: Rate constant of pseudo-second-order adsorption kinetics  
n: Adsorption intensity  
t: Time  
 $R^2$ : Correlation coefficients  
V: Solution volume  
 $V_m$ : Monolayer capacity for Langmuir isotherm  
qe: Amount of adsorbed  $Cu^{+2}$  per unit resin mass  
q: Total ion exchange capacity  
qe: Experimental value for amount of  $Cu^{+2}$  adsorbed per unit resin mass  
qe,: Calculated value for amount of adsorbed heavy metal per unit resin mass  
qt: Amount of heavy metal adsorbed at time t

## Materials

**Amberlite resins:** TP260H, SK112H and DMSCH (Lenntech) are the trade name of the sulfonated polystyrene cation exchange resins. The specifications of the resins by the supplier (Lenntech) are given in Table 1. An attempt was made during the present investigation to quantify and analyze concentrations of heavy metals in water and sediments of Kalpani stream was analyzed by means of a Varian atomic-absorption-spectrophotometer. The data is presented in Table 2. All glasswares were soaked in 0.1% Alconox solution for 24 h and rinsed with de-ionized water, and then immersed in 10% solution of  $HNO_3$  overnight.

## Sample preparations

To convert all the  $Na^+$  forms to  $H^+$  forms, 10 gram of each sample were taken and treated with 0.1 M HCl in separate burettes. All the three resins were washed several times with doubly distilled water separately in burettes and allowed to air dry, provided with a glass wool plug. The resin was conditioned by treating several 100 mL portions of 0.1 M HCL. The treatment continued until the concentration of the effluent also become equal to one molar solution. The system was then left standing for 24 hours and washed until the washing was free of  $H^+$ . After air-drying, the resin was stored for adsorption studies.

## Isotherm studies

The concentration of the  $Cu^{2+}$  ions in the aqueous phase was measured spectrophotometrically (Optima, SP-300 spectrophotometer, Tokyo, Japan) without the addition of reagents at a wavelength of 580 nm. A 1000 mg/L stock  $Cu^{2+}$  ion solution was prepared by dissolving 3.93 g  $CuSO_4 \cdot 5H_2O$  (Sigma-Aldrich, USA) in sufficient doubly distilled water to make one liter of the solution. The adjustments for different values of pH were carried out using 0.1 N sodium hydroxide (NaOH) and hydrochloric acid (HCl). Without resins control samples were run in parallel. A shaker with 24 h agitation was provided to the  $CuSO_4$  solution continuously, then the equilibration pH of the suspension was measured, centrifuged and filtered through 0.5 mm nylon filter. The adsorbed  $Cu^{2+}$  ion concentration on cationic resins were calculated by difference from the test and control concentrations of the solutions.

The concentrations (20-100 mg/L and 160-240 mg/L) of different  $Cu^{2+}$  ion solutions were measured spectrophotometrically at a wavelength of 580 nm. Standard curves demonstrating absorbance versus concentrations were prepared, using the working  $Cu^{2+}$  ion solution. Controlled experiments without resins were executed in order to validate that  $Cu^{2+}$  adsorption has not been carried out by the container walls. The synthetic solution of  $Cu^{2+}$  ions was prepared on by the analytical technique of electronic process wastewater preparation guidelines (<http://www.standardmethods.org/>).

## Kinetic studies

For kinetic studies, an exactly weighed amount (0.2 g) of resins ( $H^+$  form) was mixed with 30 mL  $Cu^{2+}$  ion solution in 100 mL conical flasks. The concentration of initial  $Cu^{2+}$  ion solutions range from 25-120 mg/L  $Cu^{2+}$  ion to 160-240 mg/L  $Cu^{2+}$  ion. The pH of the solution was adjusted to the desired value 3-9 (Jenway-3505, UK). The mixture was then shaken on an end-to-end shaker at room temperature ( $20^\circ C$ ) for 24 hours, filtered and the filtrate was analyzed for  $Cu^{2+}$  ion by discussed method. Kinetic studies was performed for copper at different concentrations (100, 120 and 160 mg/L).

## Results and Discussion

### Effect of pH on ion exchange sorption of $Cu^{2+}$

The pH is one of the most important factor affecting the ion exchange process. This is partly because hydrogen ions themselves are strongly competing for adsorbate. The solution pH influences the ionization of surface functional groups. Moreover, solution pH strongly effects the speciation and adsorption availability of heavy metals.

Sorption studies of  $Cu^{2+}$  on resins at different initial  $Cu^{2+}$  concentrations, at different pH values and at a constant temperature of  $20^\circ C$  are shown in Figure 1. It can be seen from these figures, the sorption of  $Cu^{2+}$  on resins increases with the increase in the initial  $Cu^{2+}$  concentrations in the pH range 3-5. Further increase in the pH value above 5, leads to a decrease in the sorption of  $Cu^{2+}$ , which may not only due to the decrease in the active surface sites because of the formation of  $Cu(OH)_2$  but also due to the surface alteration. Similar metal hydroxide precipitation at high pH values was observed by other scientists as well [19-21].

In water, Cu was highest followed by Cd and Ni while Cr, Pb, and Zn were not detected. The heavy metal accumulation in sediments was in the order of  $Cu > Zn > Cr > Ni > Pb > Cd$ . As shown in the table.

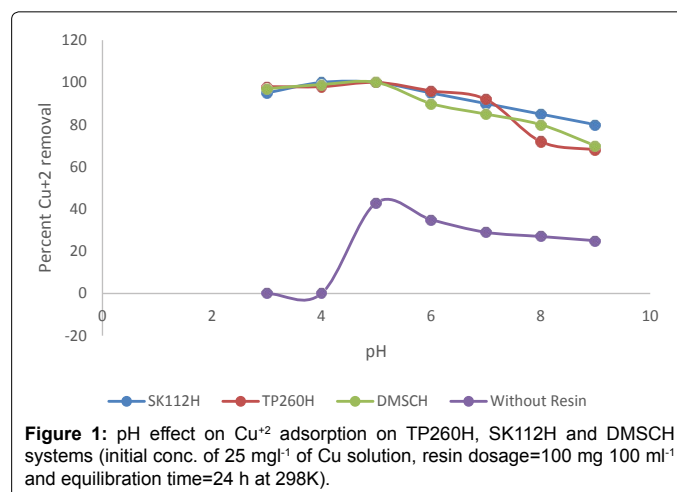


Figure 1: pH effect on  $Cu^{2+}$  adsorption on TP260H, SK112H and DMSCH systems (initial conc. of 25 mg/L of Cu solution, resin dosage=100 mg 100 ml<sup>-1</sup> and equilibration time=24 h at 298K).

Description	Lewatit® MDS TP 260	DIAION™ SK112	DOWEX™ MARATHON™ MSC
Ionic Exchange	Weakly acidic cationic exchanger	Strongly acidic cationic exchanger	Strongly acidic cationic exchanger
Ionic Form	Na+	Na+	Na+
Moisture	45-51%	49-55%	45-51%
Matrix	Aminomethylphosphonic acid	styrene-divinylbenzene (gel)	styrene-divinylbenzene (gel)
Loss on drying	~5%, 110°C	~6%, 110°C	≤ 1.2%, 110°C
Operating pH	1-12	0-14	0-14
Operating temperature	80°C (max)	120°C (max)	150°C (max)
Density	approx. 1.21 g/ml	855 g/ml	1.28 g/ml
Particle size	420 ± 50 µm	650 ± 50 µm	550 ± 50 µm
Contact time	20 mins (approx.)	20 mins (approx.)	20 mins (approx.)
Capacity	1.7 meq/mL	≥ 2.1 meq/mL	≥ 1.6 meq./mL

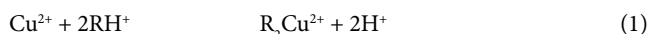
Table 1: Characteristics of the cationic exchangers used in the study.

Metal	S1 (w/s)	S2 (w/s)	S3 (w/s)	S4 (w/s)	S5 (w/s)	Mean/SD	ERL	TEL	ERM	PEL
Ni	0.020/0.583	0.043/0.571	0.060/0.652	0.0058/0.555	0.0123/0.45	0.02822 ± 0.093	30	18	145	91.3
Zn	-1.682	-1.873	-1.565	-1.663	-1.815	0.2196 ± 0.1003	120	123	270	315
Cr	-0.803	-1.568	-0.971	-0.955	-1.003	0.6 ± 0.0576	80	37.3	145	90
Cu	0.0005/2.714	-3.113	-3.098	0.0001/2.661	-3.058	0.0003 ± 0.0002	70	35.7	390	197
Pb	0.0001/0.099	-0.068	-0.067	-0.045	-0.036	0.063 ± 0.00345	35	35	110	36
Cd	0.0012/0.005	0.0051/0.006	0.0267/0.013	0.0010/0.006	0.071/0.012	0.0084 ± 0.0056	5	0.59	9	3.53

Note: S (sample), w/s (water and sediment); SD (Standard deviation); ‘-’ (Not detected); ERL (effects range low); PEL (Probable effect level); TEL (threshold effect level); ERM (effects range median); CV (Coefficients of variation); Threshold effect level [25].

Table 2: Heavy metal concentrations in water/sediments (µg/g).

Ayhan et al. [20] proposed that sorption process is preceded by the following mechanisms: (1) Ion exchange reaction. (2) physical adsorption, (3) molecular sorption of electrolytes. (4) complex formation between the counterion and the functional group. (5) hydrate formation at the surface or in the pores of the adsorbent. Here the ion exchange sorption mechanism for Cu<sup>2+</sup> can be described with the following reaction:



where RH<sup>+</sup> denotes cation exchanger and Cu<sup>2+</sup> and H<sup>+</sup> represent cations with their valency number 2 and 1 respectively.

### Effect of contact time

The effect of contact time on 15H, IRN 77H, IRN 97H and 1200H while copper being adsorbed was calculated by taking 20 ml of copper salt solution and 0.1 g of the resin in different stoppered flasks. While these flasks were shaken in the temperature-controlled shaker (at 20 ± 1°C, Vision Scientific Co., Ltd., KMC 8480S) for different time intervals. The contact time for different resins for the adsorption of copper is given in the Figure 2. With the passage of time, the removal of Cu<sup>2+</sup> ions increased from the aqueous solution possibly due to metal ions' monolayer coverage on adsorbent's surface and attained the equilibrium within 4 h for all the four resins [18].

### Effect of resin dosage on adsorption of copper

The quantity of metal taken up by a resin is a function of both the concentration of the metal and the temperature. The amount of metal adsorbed is determined as a function of the concentration at a constant temperature is explained in adsorption isotherms. Equations that are often used to describe the experimental isotherm data developed by Freundlich and Langmuir were used. Resin dosage was taken from 0.030 to 0.600 g and equilibrated for 24 h. As shown in Figure 3.

Our study showed that for the max. removal of Cu<sup>2+</sup> a minimum resin dosage of 95 mg/100 ml each of SK112H, DMSCH and TP260H

is required. Our results demonstrated that for removal of Cu<sup>2+</sup> ions all the resins had efficient performance but at certain optimum level. Beyond this level, the resin dosage increase had no significant effect on Cu<sup>2+</sup> removal [22,23]. For a given Cu<sup>2+</sup> initial concentration, with the increase of resin dosage, the equilibrium concentration decreased because greater surface sites or surface area was available [23].

### Freundlich isotherm

The empirical adsorption model, Freundlich equation for the ion exchange sorption of cations is given in the form [24]:

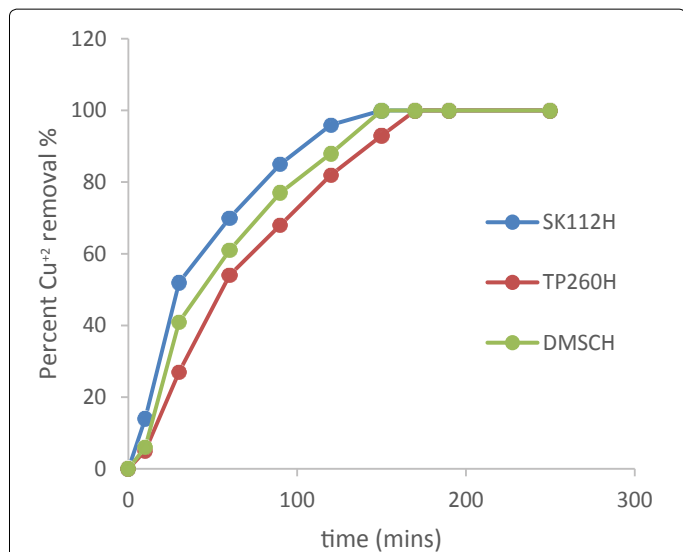
$$q_e = K C_e^{1/n} \quad (2)$$

Where q<sub>e</sub> is the amount of Cu<sup>2+</sup> equilibrium adsorption uptake concentration (mg/g), C<sub>e</sub> is the equilibrium concentration of Cu<sup>2+</sup>, K and n are empirical constants, representing the sorption capacity and intensity of sorption respectively. K is an important constant used as the relative measure for sorption efficiency. The magnitude of the n shows an indication of the favorability of sorption. Values of n larger than 1 show the favorable nature of sorption.

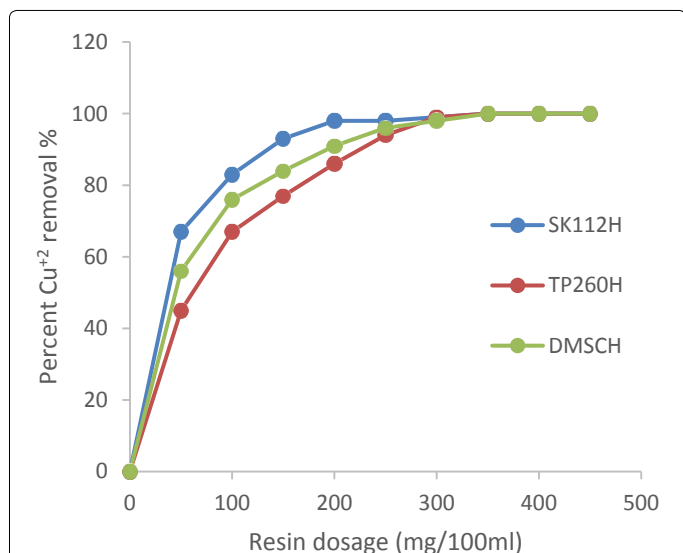
The logarithmic form of the equation 2 is:

$$\log q_e = \log K + 1/n \log C_e \quad (3)$$

Figure 3a and Table 4 demonstrated that the data for sorption of Cu<sup>2+</sup> onto Amberlite resins TP260H, SK112H and DMSCH fitted well to the Freundlich equation. These results show that the values of sorption capacity (K) are high when that pH of the solution is low while the values of K decrease when the pH of the solution becomes greater than 5. The values of intensity of sorption (n) follow the same trend and also decrease when the pH of the solution becomes greater than 5. This decrease in both the values of K and n when the pH of the solution becomes greater than 5 may not only due to the decrease in the active surface sites because of the formation of Cu(OH)<sub>2</sub> but also due to the surface alteration. Moreover, a higher value of K indicates a higher affinity for these metals.



**Figure 2:** Contact time effect on Cu<sup>2+</sup> removal by cationic exchange resins: SK112H, TP260H and DMSCH systems.



**Figure 3:** Resin dosage effect on Cu<sup>2+</sup> ion removal by cationic exchange resins: SK112H, DMSCH and TP260H.

### Langmuir isotherm

The Langmuir equation for the ion exchange sorption of cations is given in the form:

$$\frac{C_e}{q_e} = \frac{1}{kV_m} + \frac{C_e}{V_m} \quad (4)$$

where  $q_e$  is the amount of Cu<sup>2+</sup> sorbed per unit resin (mg/g),  $C_e$  is the equilibrium concentration of Cu<sup>2+</sup> (mg/L),  $V_m$  is the sorption maximum and  $K$  is the sorption energy constant. From the slope  $V$  and  $k$  can be determined.

Table 3 and Figure 4 demonstrates the linear plots of  $C_e/q_e$  vs  $C_e$ , indicating that the sorption data of Cu<sup>2+</sup> onto IRN 77H, SK112H and DMSCH obeys the Langmuir equation. These tables show that the values of sorption energy constant ( $K$ ) are high at low pH of the solution while the values of  $K$  decrease when the pH of the solution becomes greater than 5. However, the variation of  $K$  with pH is more

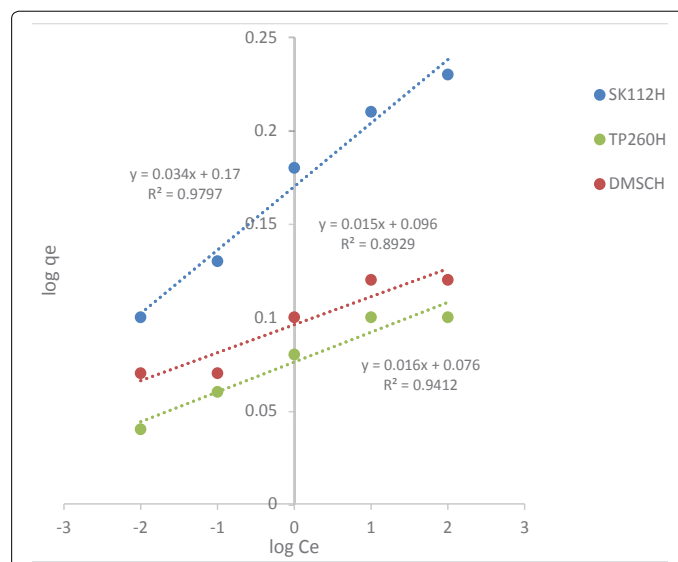
justified at low initial concentration range (25-120 mg/L). The values of sorption maxima ( $b$ ) almost follows the same trend. As stated earlier, the decrease in both the values of  $K$  and  $V_m$  when the solution pH becomes greater than 5 may not only due to the decrease in the active surface sites because of the formation of Cu(OH)<sub>2</sub> but also due to the surface alteration.

### Dubinin-Radushkevich (D-R) isotherm

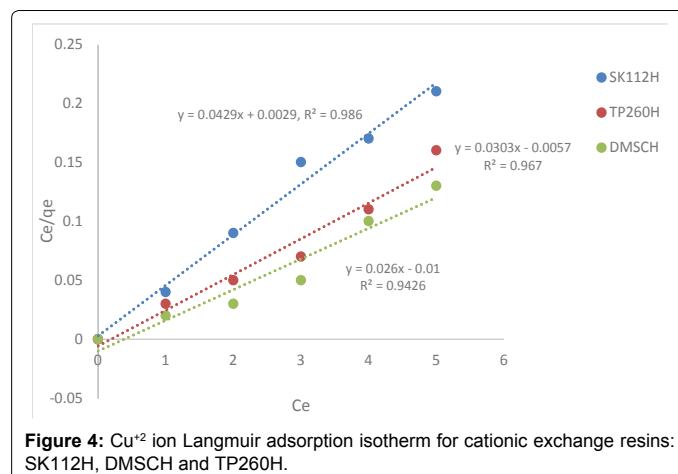
Due to the insufficiency of Freundlich and Langmuir isotherms; Dubinin-Radushkevich (D-R) isotherm was also used for the determination of copper sorption over resins. Although (D-R) isotherm is analogous of Langmuir isotherms but it rejects the constant absorption potential and homogeneity of the surfaces [24].

$$q_e = q_s \exp(-Be^2) \quad (5)$$

Where, "B" is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the biomass from infinite distance in the solution and  $q_s$  is the Dubinin-Radushkevich isotherm constant related to the degree of sorbate sorption by the sorbent surface. All the other parameters are discussed previously. Now the correlation of gives rise to;



**Figure 3a:** Cu<sup>2+</sup> ion Freundlich adsorption isotherm for cationic exchange resins: SK112H, DMSCH and TP260H.



**Figure 4:** Cu<sup>2+</sup> ion Langmuir adsorption isotherm for cationic exchange resins: SK112H, DMSCH and TP260H.



Isotherm	Freundlich, $q_e = K_f C_e^n$			Langmuir, $q_e = Q_0 C_e / (1 + b C_e)$			Dubinin-Radushkevich, $q_e = q_s \exp(-B \epsilon^2)$		
	$K_f / \text{mg g}^{-1}$	$n$	$R^2$	$Q_0 / \text{mg g}^{-1}$	$b / \text{l mg}^{-1}$	$R^2$	$q_s / \text{mg g}^{-1}$	$E$	$R^2$
SK112	13.17	0.55	0.999	28.111	3.05	9.935	32.71	1.15k	9.922
TP260	14.44	0.49	0.995	46.799	0.53	9.947	28.31	1.23k	9.991
DMSCH	12.63	0.74	0.993	35.03	2.49	9.989	30.7	1.26k	9.966

Table 3: Summary of various isotherms for Cu<sup>2+</sup> on SK112H, TP260H and DMSCH cationic exchange system.

Cu <sup>2+</sup> (mg/dm <sup>3</sup> )	SK112H			TP260H			DMSCH		
	10	15	20	10	15	20	10	15	20
<sup>1</sup> k <sub>i</sub> (l/hr)(R <sup>2</sup> )	0.5123 (0.9822)	0.4853 (0.9877)	0.6225 (0.9329)	0.6255 (0.9807)	0.5577 (0.9807)	0.4368 (0.9922)	0.4115 (0.9455)	0.6531 (0.9677)	0.4455 (0.9693)
<sup>2</sup> k (g/mg·min)(R <sup>2</sup> )	0.0245 (0.9888)	0.0255 (0.9631)	0.0296 (0.9988)	0.0122 (0.9989)	0.0277 (0.9776)	0.0125 (0.9669)	0.0352 (0.9843)	0.0279 (0.9236)	0.0303 (0.9566)
<sup>3</sup> h (mg/g)	5.5538	8.0012	11.2335	4.276	6.2132	9.342	3.443	5.1125	7.1227
<sup>4</sup> K <sub>id</sub> (mg/g·hrs <sup>1/2</sup> )(R <sup>2</sup> )	4.6698 (0.9845)	6.5121 (0.9888)	8.0091 (0.9180)	7.1056 (0.9678)	8.0599 (0.9767)	9.035-0.9905	4.2200 (0.9540)	5.6029 (0.9007)	6.9142 (0.9354)

<sup>1</sup>Pseudo 1<sup>st</sup> order rate constant, <sup>2</sup>Pseudo 2<sup>nd</sup> order rate constant and <sup>3</sup>Initial Cu<sup>2+</sup> sorption rate constant, <sup>4</sup>Intraparticle rate constant.

Table 4: Pseudo first, second order and intra-particle diffusion values at different initial Cu<sup>2+</sup> concentrations on SK112H, TP260H and DMSCH cationic exchange system.

$$\epsilon = RT \ln[1 + 1/C_e] \quad (6)$$

Where 'T' is the absolute temperature and 'R' is a gas constant, 'B' gives off free mean energy E of sorption/molecule i.e., The plot of  $\ln q_e$  vs  $\epsilon^2$  helps in the calculation of the constants E and q<sub>s</sub>.

$$E = 1/(2B)^{1/2} \quad (7)$$

The results showed that all the three resins had nearly same sorption energy/sorbate. The removal of Cu<sup>2+</sup> through resins may be due to ion exchange. As shown in Figure 5. Cupric ion readily taken by Amberlite synthetic ion exchange resins are well established by numerous studies. [5-7,25] The different components of resins include sulphonates due to these polymeric components these materials can capture copper ions efficiently. One of the speculations includes that these resins contain sulphonates that actively attracts cations.

Alyuz et al. [19] studied the removal of zinc and nickel on Dowex HCR S/S cation exchange resin from aqueous solutions as a function of pH (2-9), the dosage of resin (0.05-7 g) and contact time. They observed that adsorption percentage of metal ions increased with increasing resin dosages which may be due to the formation of greater adsorption sites or surface area. Similarly, the percentage of metal ions increased with increasing the time and attained equilibrium in 90 min for nickel and in 120 min for zinc, indicated that complete removal of Ni<sup>2+</sup> ions required less residence time compared to Zn<sup>2+</sup> ions. Similar conclusions were drawn by other investigators [20,22,23]. They also concluded that optimal removal of Ni<sup>2+</sup> and Zn<sup>2+</sup> occurred at pH 4 and 6 respectively.

At high pH values, the decrease in removal efficiency achieved by resin may be described with the formation of Ni(OH)<sub>2</sub> and Zn(OH)<sub>2</sub> during the interaction of Ni<sup>2+</sup> and Zn<sup>2+</sup> ions with OH<sup>-</sup>. In this state, hydrolysis accompanied by precipitation of metal hydroxides may occur [24].

Rengaraj et al. [15] studied the removal of Co<sup>2+</sup> from water and wastewaters on various ion exchange resins (IRN77 and SKN1) as a function of initial metal-ion concentration (10-150 mg/L). They found that amount of Co<sup>2+</sup> removal increased with increasing concentration of the solution. Similar increase in other heavy metals removal from aqueous solution with the increase in concentration was found by other workers [18,21,23]. They also observed that IRN77 cation exchange resin may be used as an adsorbent for the effective removal of Co<sup>2+</sup> from aqueous solution due to its higher ion exchange capacity

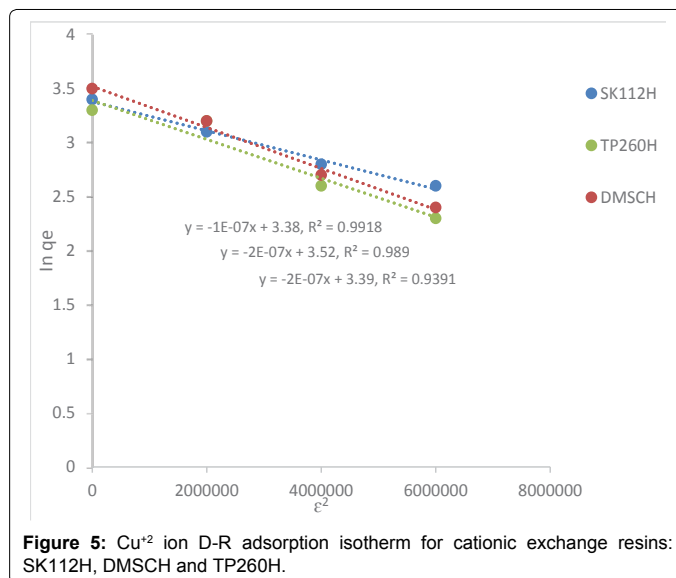


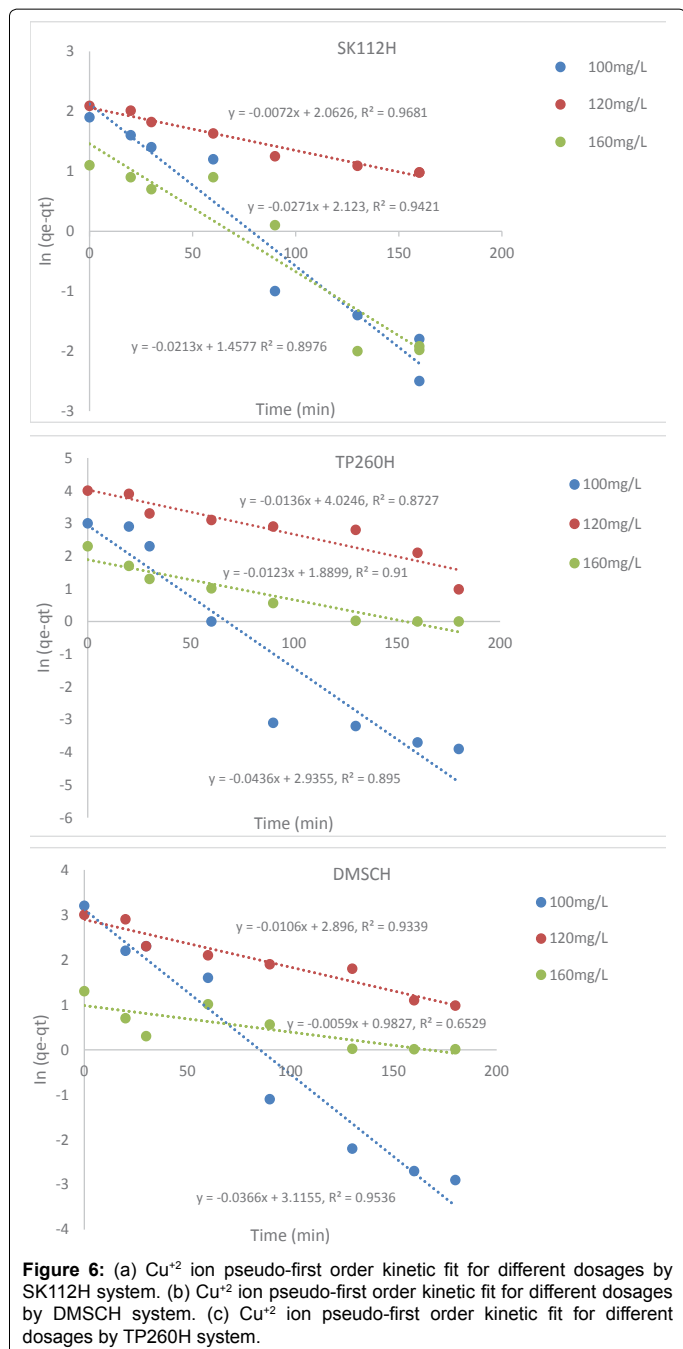
Figure 5: Cu<sup>2+</sup> ion D-R adsorption isotherm for cationic exchange resins: SK112H, DMSCH and TP260H.

(>1.9 eq. L<sup>-1</sup>) than that of SKN1 (<1.7 eq. L<sup>-1</sup>). Cu<sup>2+</sup> and the values of n greater than 1, indicating favorable sorption. A similar conclusions were drawn by McKay et al. [15].

Incase of ion exchangers of different functional groups [25-27], the selectivity order for alkali metal cations followed the well-known lyotropic series as in case of polystyrene-sulphonic cation exchangers. However, as was shown by Bregmann [25] and Tien [27], a complete reversal of this order was observed with the resins having carboxyl and phosphonate fixed groupings. Further, in both these ion exchangers the selectivity was found to be pH dependent. In the case of phosphonic acid exchanger [27], at low pH values, where the ionic group was -PO<sub>3</sub>H, Cs<sup>+</sup> was strongly preferred over Rb<sup>+</sup> but at high pH values, where presumably the ionic group was -PO<sub>3</sub><sup>2-</sup>, Li<sup>+</sup> was preferred and the sequence was thus reversed.

Figures 6 and 7 show the linear plots of Ce/T vs Ce, indicating that the sorption data of Cu<sup>2+</sup> onto Amberlite resins obeys the Langmuir equation.

These tables show that the values of sorption energy constant (K) are high at low pH of the solution while the values of K decrease when the pH of the solution becomes greater than 5. However, the variation



of  $K$  with pH is more justified at low initial concentration. The values of sorption maxima (b) almost follows the same trend. As stated earlier, the decrease in both the values of  $K$  and  $V_m$  when the solution pH becomes greater than 5 may not only due to the decrease in the active surface sites because of the formation of  $\text{Cu}(\text{OH})_2$  but also due to the surface alteration.

### Kinetic studies of ion exchange sorption of $\text{Cu}^{2+}$ ions

**Adsorption kinetics:** Kinetics of adsorption were used to explain the characteristics and mechanism of adsorption.

**Pseudo-first-order reaction kinetics:** The adsorption kinetics presented for the first time by Ho [19] and Lagergreen [18] as shown:

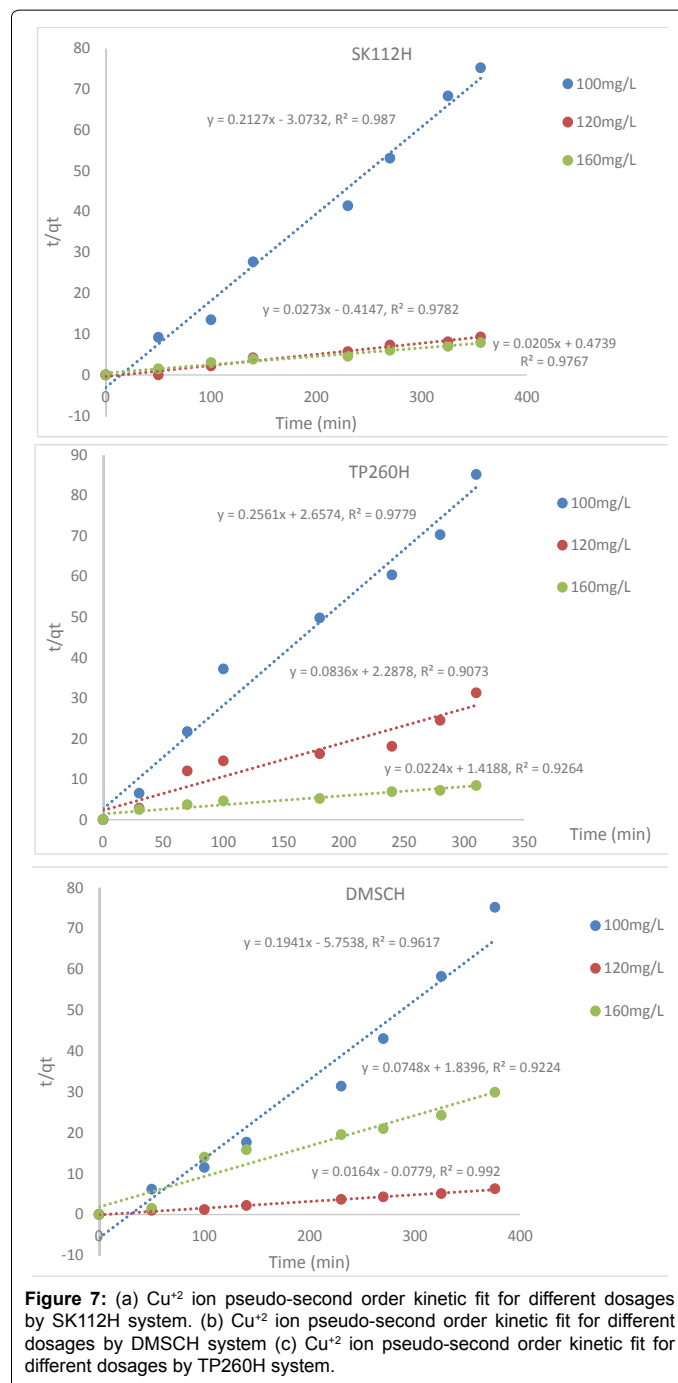
$$dq_t/dt = k_1(q_e - q_t) \quad (5)$$

where  $k_1$  is the first order rate constant for adsorption,  $q_e$  is the amount of copper ions adsorbed expressed in whereas  $q_t$  is the amount of copper ions adsorbed at time interval "t". Both expressed in units of milligrams per gram. The following expression is obtained after the integration of the above equation:

$$\ln(q_e - q_t) = -k_1 t + C_1 \quad (6)$$

where  $C_1$  is the first order integration constant. If suppose,  $q=0$  at  $t=0$ , then:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$



**Pseudo-second-order reaction kinetics:** Pseudo second order reaction was also used to evaluate the adsorption kinetics [20]:

$$dq_t/dt=k_2(q_e-q_t)^2 \quad (8)$$

where  $k_2$  is the constant for second order kinetics. By the integration of Eq.(8), we get the following expression:

$$1/(q_e-q_t)=k_2t + C_2 \quad (9)$$

Where  $C_2$  is the second order integration constant. Algorithmic arrangement of equation gives the following expression:

$$t/qt=1/k_2q_e^2 + t/qe \quad (10)$$

In our study, we used the initial concentrations of copper as 20, 100 and 180 mg/L respectively. The adsorption rate constants for copper was calculated using pseudo first and pseudo second order rate equations. The plots  $\ln(q_e-qt)$  against time showed linear curves. The pseudo first order kinetics and pseudo second order kinetics for copper adsorption onto resins are shown in Figures 6 and 7. The calculation of rate constants,  $k_1$  and  $k_2$  were done from the curve slopes. As shown in Table 4.  $Cu^{+2}$  pseudo-second order chemical reaction kinetics provide the best correlation of the experimental data for 1200H, whereas the pseudo-first order model proposed fits the experimental data well for SK112. The mechanism of chromium adsorption included intraparticle diffusion process for resins. One of the studies demonstrated that due to increasing in adsorbent particle size, the adsorption percentage decreased as well [27]. Our study showed similar results.

**Intraparticle diffusion model:** The intraparticle diffusion ( $k_{id}$ ) rate constant is given as:

$$q=k_{id}t^{1/2} \quad (11)$$

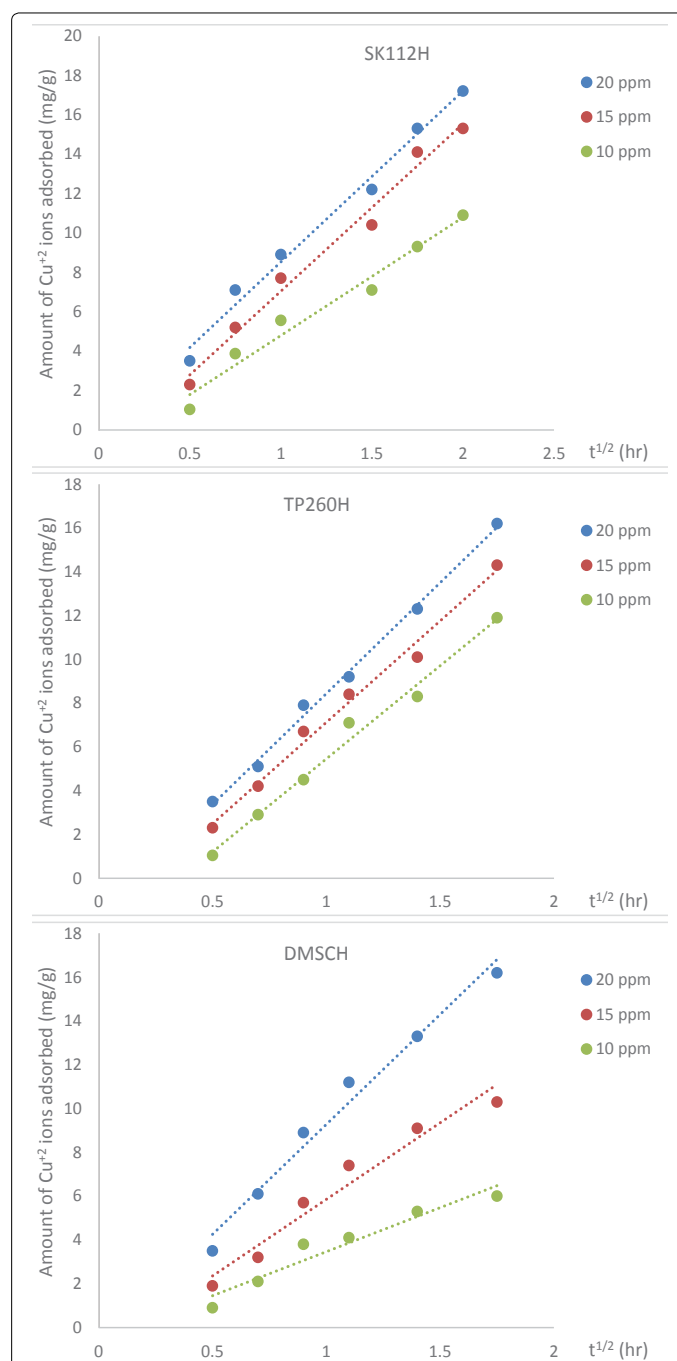
where the values of  $k_{id}$  were calculated from the linear proportion slope for each metal ion concentration, the amount adsorbed  $q$  expressed in terms of (mg/g) at given time interval,  $t$  (hrs). For different initial concentrations, the plots for TP260H, SK112H and DMSCH of 'q' versus ' $t^{1/2}$ ' are shown in Figure 8.

At high concentration, the value of  $k_{id}$  was higher.  $Cu^{+2}$  ion transportation and diffusion is quite easier into TP260H as compared to SK112H and DMSCH. As a result it has high diffusion rates.  $Cu^{+2}$  ions are adsorbed by surface of the cationic resins. When the saturation is achieved by the external surfaces of resins;  $Cu^{+2}$  is adsorbed by the internal surfaces.  $Cu^{+2}$  ions diffuses into the cationic resins, diffusion resistance is increased, rate of diffusion decreases. By the decrease in concentration of solution of  $Cu^{+2}$ , the decrease in diffusion rate occurs and ultimately equilibrium is attained. By the increase in initial concentration of  $Cu^{+2}$ , the initial sorption rate and intraparticle diffusion rate as was also increased.

The use of synthetic ion-exchange resins in pharmaceutical industries has been diffused and varied. Historically, natural ion-exchange resins like bentonite, kaolin, alumina, alginates and charcoal were commonly used for many industrial applications. The recent advancement in synthetic IR lead to the development of some novel medical and pharmaceutical applications. They are now not only used as a water purification tool, active ingredient and excipients; they are used for the purification and extraction of enzymes, alkaloids, fermentation of various products, antibiotics, hormones and viruses etc. They meet the requirements of the British (BP), European (Ph. Eur.), American (USP), and Japanese (JP) Pharmacopoeias for the preparation of various controlled release drug formulations.

Most of our knowledge about ion exchange is derived from numerous investigations that have been made to study the selectivities, rates, and thermodynamics of simple cation exchange processes. However, comparatively very little data is available about the sorption of cations on strong cation exchangers. Selectivity is the ability to choose some ions rather than others.

Ion exchange separations are mostly based on selectivity and find significant importance for predicting the course of ion-exchange reactions and their practical applications.



**Figure 8:** (a) Intraparticle diffusion plot for  $Cu^{+2}$  ion adsorption on TP260H system (b) Intraparticle diffusion plot for  $Cu^{+2}$  ion adsorption on SK112H system. (c) Intraparticle diffusion plot for  $Cu^{+2}$  ion adsorption on DMSCH system.

The factors affecting the ion-exchange selectivity are charges of ions being exchanged, types of functional groups as well as specific interactions in the ion exchanger, composition of ion exchanger phase, crosslinking, temperature, formation of complexes in the solution, solvation, swelling etc. Functional groups of most commonly used strongly acidic cation exchangers ( $\text{SO}_3^-$ ) and strongly basic anion exchangers  $[-\text{CH}_2\text{N}(\text{R}_1\text{R}_2\text{R}_3)^+]$  show poor complex forming abilities owing to which there are observed 'normal' affinity series in which the factors responsible for the position of a given ion are its charge, radius and solvation extent [25-27].

## Conclusions

The aim of this work was to investigate  $\text{Cu}^{2+}$  sorption from aqueous solutions by using Amberlite resins. Ion exchange process was pH dependent and optimal sorption efficiency for  $\text{Cu}^{2+}$  was obtained at pH 5.4. Application of resins to wastewater treatment is expected to be economical and efficient. Freundlich, Dubinin-Radushkevich and Langmuir equations equations were found to best fit the data in the present investigation. In batch studies, the synthetic wastewater of  $\text{Cu}^{+2}$  ions removal confirms their cogency of results.  $\text{Cu}^{+2}$  removal through these resins followed pseudo second order reaction kinetics. These batch studies kinetic data is useful for the exploiting and designing of treatment plan for industrial effluents and wastewater. Our study demonstrated that these resins can be used for the efficient removal of  $\text{Cu}^{+2}$  ions from the wastewater. Resins used to remove  $\text{Cu}^{+2}$  ions may remove other heavy metals as well. In kalpani river  $\text{Cu}^{+2}$  was highest followed by Cd and Ni while Cr, Pb and Zn were not detected in water. Whereas the heavy metal accumulation in sediments was in the order of  $\text{Cu} > \text{Zn} > \text{Cr} > \text{Ni} > \text{Pb} > \text{Cd}$ . Sorption of  $\text{Cu}^{+2}$  ions in these resins and intraparticle diffusion was the key rate limiting step. Detailed studies are needed for further assessment in terms of reaction chemistry, competitive sorption and thermodynamics of ion exchange process. Our study showed that TP260H is more effective in treating waste water than SK112H or DMSCH. Also the adsorption of the Amberlite resin blends should be studied.

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