

## Comparative Studies for Adsorption Processes of Transition Element Cu(II) Ions by Macroporous Cation Exchange Resin

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### ABSTRACT

In this work the adsorption processes are carried out on Cu<sup>+2</sup> ions from aqueous solution in presence of macroporous cation exchange resin (AMBERSEP 252H) at different temperatures. The different parameters such as concentrations of metal ions, temperatures and presence of acid were studied. The obtained adsorption data fitted on the linear equation of Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich isotherm models. The effect of temperature on the adsorption was performed to evaluate the influence of Cu<sup>+2</sup> ions adsorption capacity. Additionally, thermodynamic parameters ( $\Delta H$ ,  $\Delta S$ ,  $\Delta G$ ) were determined. The removal efficiency copper ions from aqueous medium using such resin was 98.7%. Moreover, the experimental isotherm models were evaluated for the Langmuir, Freundlich, Temkin and D-R isotherms. Therefore, the correlation coefficient ( $R^2$ ) indicates the following order to fit model with adsorption mechanism of copper ions (Cu<sup>+2</sup>) onto the resin : Langmuir > D-R > Temkin > Freundlich.

**Key words** Copper, AMBERSEP 252H, adsorption, water treatment

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### Introduction

Some of transition metals are often found in industrial wastewaters, which originate from metal plating, battery manufacture, petroleum refining, paint manufacture, pigment manufacture, printing and photographic industries, etc. (Kadirvelu *et al.*, 2001).

Different metal ions is special concern as they can accumulate in different components of the environment, represent a serious threat to human lives. Cu<sup>+2</sup> ions is one of the most toxic metals. The copper Cu<sup>+2</sup> ions has been well recognized for its negative effect on the environment where it is non-degradable and accumulates readily in living systems. Adverse health effects due to cadmium are well documented and it has been reported to cause renal disturbances, lung insufficiency, bone lesions, cancer and hypertension in humans. (Xiong *et al.*, 2009) .

A number of methods have been developed over the years to remove copper Cu<sup>+2</sup> ions from water such as chemical precipitation, chemical reduction, ion exchange, membrane separation, adsorption and reverse osmosis. (Biddau *et al.*, 2005; Xiong *et al.*, 2006; Pehlivan *et al.*, 2006; Zhou *et al.*, 2004; Kaikake *et al.*, 2007 and Choy *et al.*, 2005).

Ion exchange has increasingly received more attention in environmental treatment applications throughout the world in recent years because the method is simple, relatively low-cost and effective in removing pollutant metal ions. (Tan *et al.*, 2008; Wu *et al.*, 2004 and El-Kamash, 2008). Transition metal ions are toxic elements present in waste waters from different industrial sources. (Phillips *et al.*, 2007; Wan Ngah *et al.*, 2008, O'Connell *et al.*, 2008; Srivastava *et al.*, 2009 and Gode *et al.*, 2006). Increasing presence of transition metals in ground water is a very dangerous environmental concern. (Vaughan *et al.*, 2004; Lin *et al.*, 2000; Karthikeyan *et al.*, 2005; Kendu<sup>-</sup> zler *et al.*, 2006 and Apiratkul and Pavasant, 2008).

Erdem *et al.* (2004) have been studied the removal of transition elements from industrial sources. Many investigations obtained various technologies for eliminating of pollutants, via adsorption on activated carbon, chemical precipitation, coagulation and ion exchange resin. Among of these methods, ion exchange resin which is found to be the best for removal of metal ions because of its relative simplicity of application, non-corrosive, simple regenerations and could be used several times. Different groups researched into specially adsorbents using synthetic ion exchange resin that facilitate cheap and effective chemical regeneration process (Lakshmi *et al.*, 2004 and Wang *et al.*, 2007).

The aim of this work is to investigate the performance of AMBERSEP 252H as strong cation exchange resin to remove copper ions Cu<sup>+2</sup> from aqueous medium and studies the parameters. The parameters that influenced the adsorption coefficient, such as initial metal ion concentration, temperatures, acid concentration.

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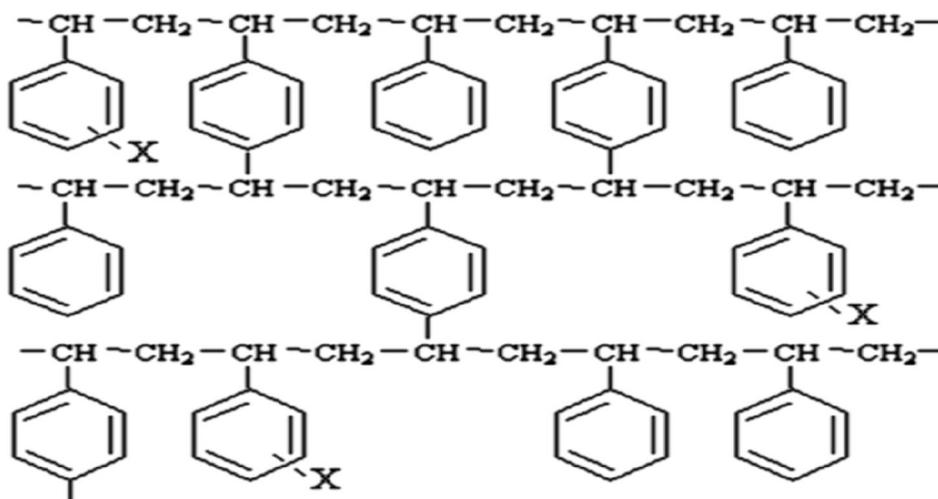
Also, experimental results will apply to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) adsorption isotherms. It is likely that this study might be give useful for treatment processes of sectors containing transition metal in their wastewaters.

**Experimental**

**Materials and methods**

Reagents were used in this study standard 0.001 M EDTA solutions, Muroxide as indicator and buffer solution. (CuCl<sub>2</sub>) were used to preparing different concentrations.

AMBERSEP 252H is a macroporous cation exchange resin based on sulphonated crosslinked polystyrene from (Rohm and Haas company, Philadelphia, U.S.A). It has a moderate degree of crosslinking resulting in good regeneration efficiency. It is very resistant to osmotic shock and mechanical attrition. The chemical structure, physical and chemical properties of AMBERSEP 252H are given in (Fig. 1) and (Table 1).



**Fig.1:** Styrene divinyl benzene co- polymer , X= inorganic functional group (SO<sub>3</sub><sup>-</sup>)

**Table 1 :** Physico-Chemical properties of tested strongly acidic AMBERSEP 252H cation exchange resin.

Characteristics	Value
Type	Styrene divinyl benzene copolymer.
Physical Form	Light gray beads
Functional group	Sulfonic group (SO <sub>3</sub> <sup>-</sup> )
Whole bead count	95% min
Ionic form, as shipped	H <sup>+</sup>
Total capacity	≥ 1.65 eq/L ( H <sup>+</sup> form)
Moisture holding capacity	52 : 58 % ( H <sup>+</sup> form)
Specific gravity	1.18 to 1.22 ( H <sup>+</sup> form)
Shipping weight	755 g /L
Particle size	
Harmonic mean size	0.90 - 1.10 mm
Uniformity coefficient	≤ 1.4
Fines content	<0.600mm : 1.0 % max
Coarse beads	>1.180 mm: 10.0% max
Maximum reversible swelling	Na <sup>+</sup> → H <sup>+</sup> : 7%

**Copper ions (Cu<sup>+2</sup>) concentration**

The element was determined in a variety of conditions including contact time and resin dosages effect on the removal of copper ions (Cu<sup>+2</sup>). Effects of each factor were determined keeping other variables constant. The solutions were diluted as required to obtain standard solutions containing 0.001–0.1 mole of metal ions. About 50 ml of metal ions in aqueous solution was taken in reagent bottles of 100 ml capacity, known amounts of 0.5 g resin was added separately in 50 ml of the above solutions. The solutions were then agitated after

appropriate intervals, 5, 30, 60, 90, 150, 210 and 270 min. for a predetermined period at 298K. The resin was separated and the filtrate was analyzed by titration with EDTA di-sodium salt as the titrant. Additionally, the adsorption process were carried out with different concentrations of HCl solutions as acid medium.

In the experiments 50 ml of synthetic solutions containing of Cu<sup>2+</sup> were added into flasks with different amounts of resin varying between 0.25 and 3g. Temperature was kept constant at 298K during batch tests, then the metal ion concentration in the solution was determined.

One millilitre solution of the metal ions was taken and diluted with cooled de-ionized water on the basis of analysis of chemical composition. Murexide indicator was used for Cu<sup>2+</sup> in the presence of buffer solution. The solution acquires a yellow colour. Titrate with standard EDTA 0.001M until there is a sharp change of colour from yellow to pink. The concentration of Cu<sup>2+</sup> before and after equilibrium was calculated by using the Cu<sup>2+</sup> factor (Wassel *et al.*, 2014)

$$\{ 1 \text{ cm}^3 \text{ of } 0.001 \text{ M EDTA} = 0.06354 \text{ mg Cu}^{+2} \}$$

The adsorption capacity was calculated using following formula (Alyüz *et al.*, 2009):

$$q_e = \frac{C_0 - C_e}{m} V \text{ ----- (1)}$$

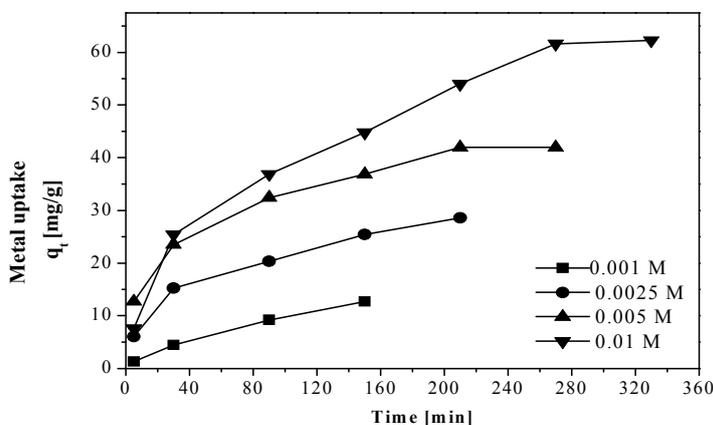
Where  $q_e$  (mg/g) is the amount of metal adsorbed at equilibrium,  $C_0$  and  $C_e$  (mg/L) are the initial and equilibrium concentration of metal ions in solution,  $V$  (L) is the volume, and  $m$ (g) is the amount of the resin. The batch distribution coefficient  $K_D$ , is defined by the following equation (Erdem *et al.*, 2004).

$$K_D = q_e / C_e \text{----- (2)}$$

## Results and Discussion

### 1. The effect of metal ions concentration on the adsorption of copper (Cu<sup>2+</sup>) ions.

Figure 2 reveals the relation between the metal ion uptake by AMBERSEEP 252H and the concentration of such metal as a function of time. The results show that, with increasing Cu<sup>2+</sup> ions concentration, the uptake of ions increase as the contact time elapsed. The equilibrium time was reached within (210-270) min (Fig. 2). The kinetic curves are single and continuous, indicating the possible monolayer coverage of metal ions on the surface of the adsorbent. This description agrees well with Aroua *et al* work(Aroua *et al.*, 2008).



**Fig. 2:** quantity of adsorbed Cu<sup>2+</sup> ions on the surface of adsorbent (resin) at different concentrations of copper ions.

The adsorption of copper (Cu<sup>2+</sup>) ions onto the AMBERESEEP 252H strong acid cation exchange resin at 298K was rapid for the first 30 min. However, the equilibrium was reached within 270 min. The time profile of metal uptake is a continuous curve leading to saturation. Crini *et al.* reported that the adsorption mechanisms are complicated because a large number of interactions, such as ion exchange, physical adsorption and hydrophobic interactions are involved (Crini *et al.*, 2010). It can be concluded that metal ions removal rapidly increases within the time due to fast interactions between metal ions and the surface of the adsorbent and keeps increasing gradually until the equilibrium is reached then the concentration remains constant. To discuss this behavior, the

affinity between the adsorbent (resin) and the adsorbate ( $\text{Cu}^{+2}$ ) ions has to be considered. It is the main interaction force for controlling the adsorption process (Crini *et al.*, 2010).

The adsorption isotherms are shown in (Fig. 2). It is found that the curve initially rises sharply indicating that a large quantity of active sites are available in the beginning of the adsorption process. However, the AMBERSEP 252H resin becomes saturated because the active sites were consumed. This increase of the adsorption capacity with the metal ions concentrations increased can be explained with the high driving force by a higher concentration gradient. In general, the high concentrated the solution lead to good adsorption (Demirbas *et al.*, 2005 and Wassel *et al.*, 2014).

2. The effect of temperatures on the adsorption of copper ( $\text{Cu}^{+2}$ ) ions.

The pore size of the adsorbent might be changed with temperature leading to modify the adsorption rate. Otherwise, the variety of the temperature probably used to enhancement in the chemical affinity of the metal ions to the surface of the adsorbent leading to some kind of chemical interaction takes place during the adsorption process. Therefore, the adsorption capacity increase with increasing temperature (Fig.3).

At higher temperatures, the possibility of diffusion of solute within the pores of the adsorbent may ruled as reported by workers (Krishanan *et al.*, 2002).

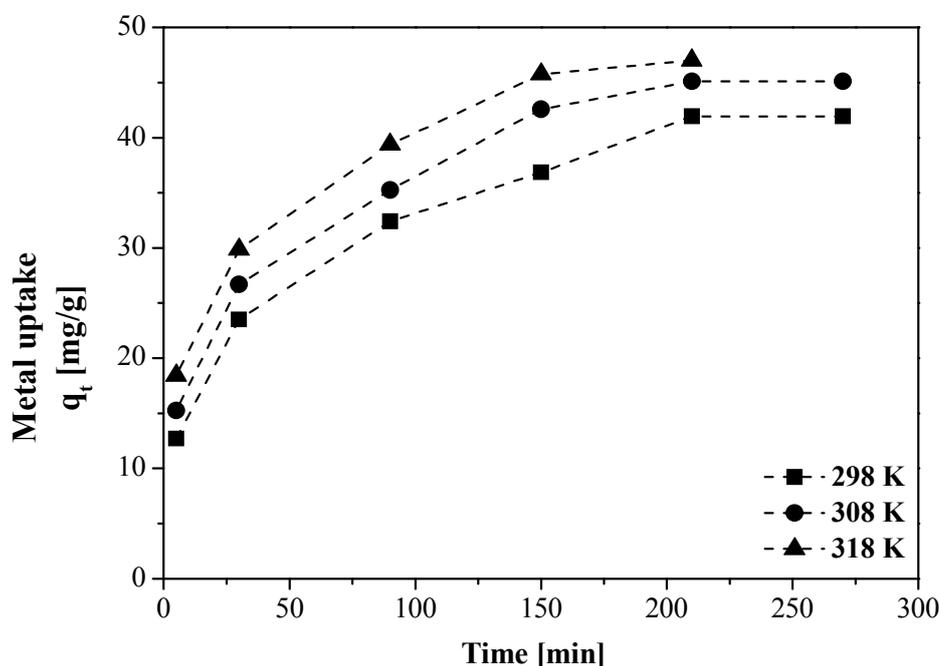


Fig. 3: Amount of  $\text{Cu}^{+2}$  ions adsorbed on the surface of resin at different Temperatures.

The diffusion is an endothermic process. Therefore, a greater adsorption will be observed at high temperature. Thus, the diffusion rate of metal ions in the external mass transport process increases with temperature. The effect of temperature on adsorption is further confirmed by the Vant Hoff plots (Fig.4) (Xionga *et al.*, 2011, Jeong *et al.*, 2011 and Liua *et al.*, 2011) and illustrate in the following equations (3,4,5 and 6):

$$K_D = q_e / C_e \quad \text{----- (3)}$$

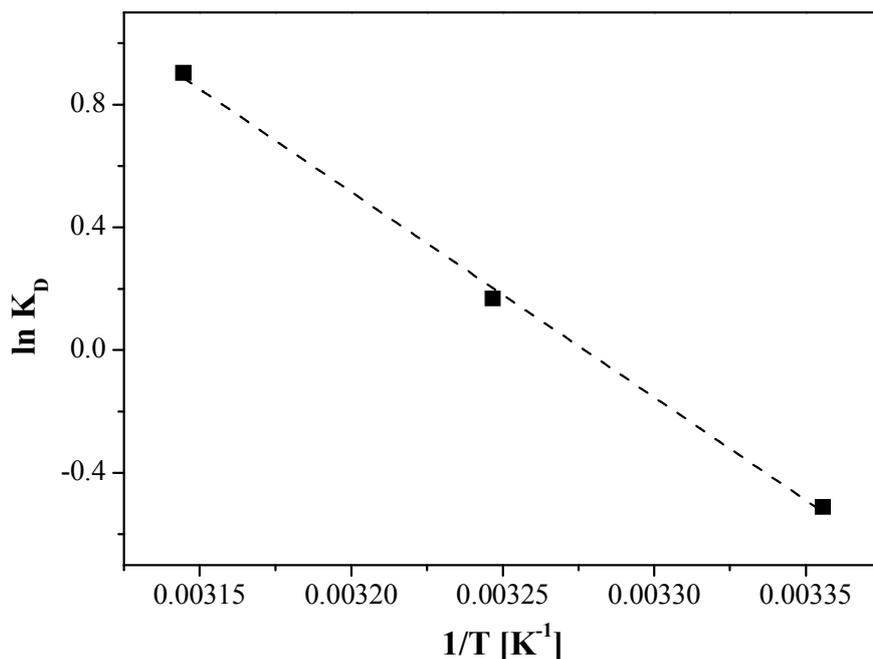
$$\Delta G = - RT \ln K_D \quad \text{----- (4)}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{----- (5)}$$

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \text{----- (6)}$$

Where T is absolute temperature in Kelvin (K), R is the gas constant (8.314 j/mol K) and  $K_D$  is the distribution coefficient (ml/g).

The thermodynamic parameters namely enthalpy change ( $\Delta H$ ) and the entropy change ( $\Delta S$ ) can be calculated from the slope the intercept of the straight line plotted by  $\ln K_D$  versus  $1/T$ , as in (Fig. 4).



**Fig. 4:** Van't Hoff diagram for adsorption between copper ions and AMBERSEP 252H

The Gibbs free energy change ( $\Delta G$ ) was determined at 298, 308 and 318 K. The obtained thermodynamic parameters were listed in (Table 2).

**Table 2:** Thermodynamic parameters for  $\text{Cu}^{+2}$  ions

Slope	Intercept	$\Delta S(\text{KJ/mol})$	$\Delta H (\text{J/mol})$	$\Delta G (\text{KJ/mol})$	
				Temp.	Value
-6693.17	21.93315	182.3522	55.647	298 K	431
				308 K	1265
				318 K	2387

The adsorption abundant of  $\text{Cu}^{+2}$  ions onto the surface of AMBERSEP 252H resin were observed, because the number of  $\text{H}^+$  ions attached to activate sites of the adsorbent decreased. Therefore, the positive value of  $\Delta S$  suggested some structure changes in the adsorbent and adsorbate. In fact, the positive value of enthalpy  $\Delta H$  further confirmed the endothermic nature of the process, so increasing temperature supplied with a more favorable adsorption of  $\text{Cu}^{+2}$  ions onto the adsorbent (AMBERSEP 252H). The positive Gibbs free energy values for  $\text{Cu}^{+2}$  ions adsorbed on the adsorbent at 298 K indicates the presence of an energy barrier in this process illustrated in Ref. (Sharma and Neetu, 2011), while the increase of temperature results in the decreasing values of these thermodynamic parameters indicating the feasibility of the process.

*3. The effect of mineral acidic medium on the adsorption of copper ( $\text{Cu}^{+2}$ ) ions.*

The water pollutants were obtained via industries such as acidic, basic and organic compounds. Therefore, the adsorption process were carried out with different concentrations of HCl solutions as acid medium to investigate the efficiency of such resin to remove the metal ions from water. The result show that the maximum uptake of  $\text{Cu}^{+2}$  ions occurred at the lowest concentration of HCl acid . However, the uptake of metal ion decreased with increasing of acid media as shown in (fig.5), and agreeing well with Phillips *et al.* work (Phillips *et al.*, 2007).

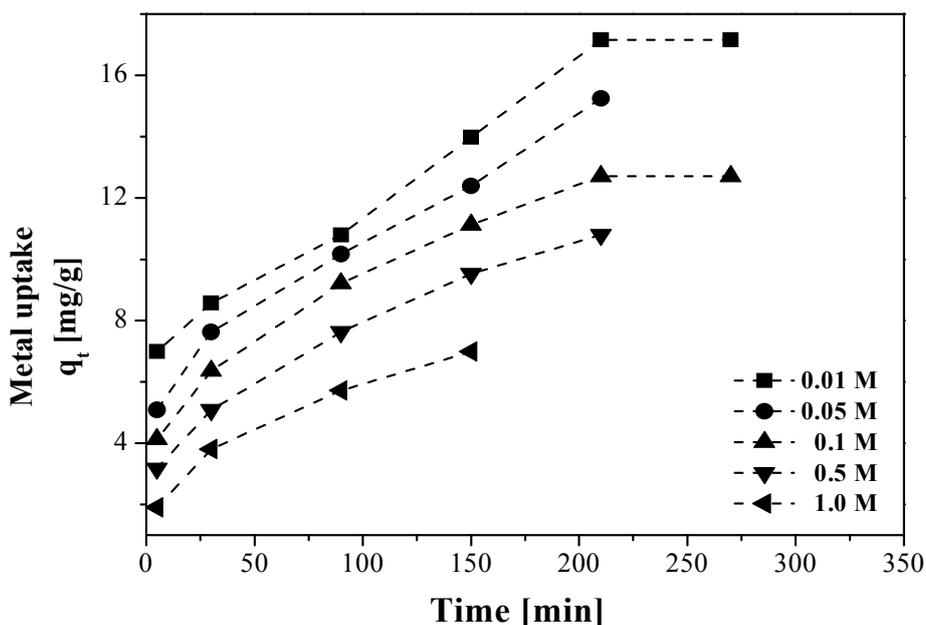


Fig. 5: Metal uptake in acidic medium (HCl) at different Concentrations.

An increase in acid from 0.01 to 1.0 M considerably lowers the uptake values, this change can be explained as the ability of the copper ions ( $\text{Cu}^{+2}$ ) to form negatively charged ions increases. The respective adsorption value proceeds according to the following order of the total molar solution  $0.01 > 0.05 > 0.1 > 0.5 > 1.0 \text{ M}$ . This effect is different from metal to metal depending on the stability of the dominant acid-complex species in the condition concerned. Such effect generally means that the acidity group competes more effectively in the exchange sites as Hydrochloric acid concentration increases and the activity coefficient, which it increases with decreasing concentration (0.01–1.0 M) (Phillips *et al.*, 2007)

4. Study The Adsorption Isotherm Models

A- Langmuir Isotherm

The Langmuir isotherm is a model for adsorption on a completely homogenous surface with negligible interaction between adsorbed molecules (Gode and Pehlivan, 2005). The model assumes uniform adsorption energies onto the surface and maximum adsorption depends on saturation level of monolayer.

Langmuir model has a correlation coefficient ( $R^2 \approx 0.998$ ). This indicates that the model is fitting with adsorption mechanism of metal ions on the surface of resin. Langmuir adsorption model represented as the following equation (7). (Langmuir, 1918).

$$C_e q_e = (1/k V_m) + (C_e/V_m) \text{----- (7)}$$

Where  $q_e$  represents the mass of adsorbed copper ions per unit weight of resin (mg/g),  $V_m$  is the monolayer capacity,  $k$  is the equilibrium constant and  $C_e$  is the equilibrium concentration of the solution (mg/L).  $k$  and  $V_m$  were determined from the slope, intercept of the Langmuir plot as shown in (Fig.6).

B- Freundlich Isotherm.

The Freundlich model is known as earliest empirical equation and is shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surfaces (Ho, 2005 and Veliev *et al.*, 2006).

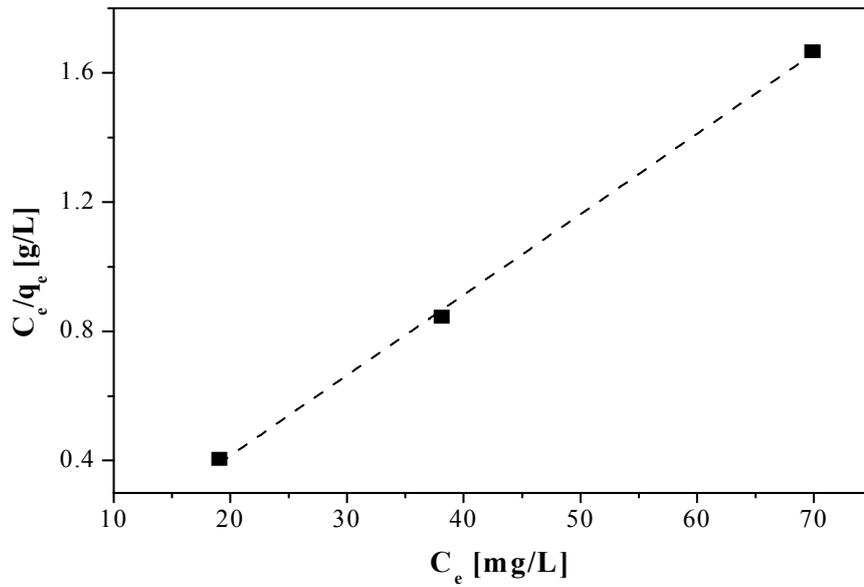


Fig. 6: Langmuir isotherm for copper ions adsorbed on the surface of resin.

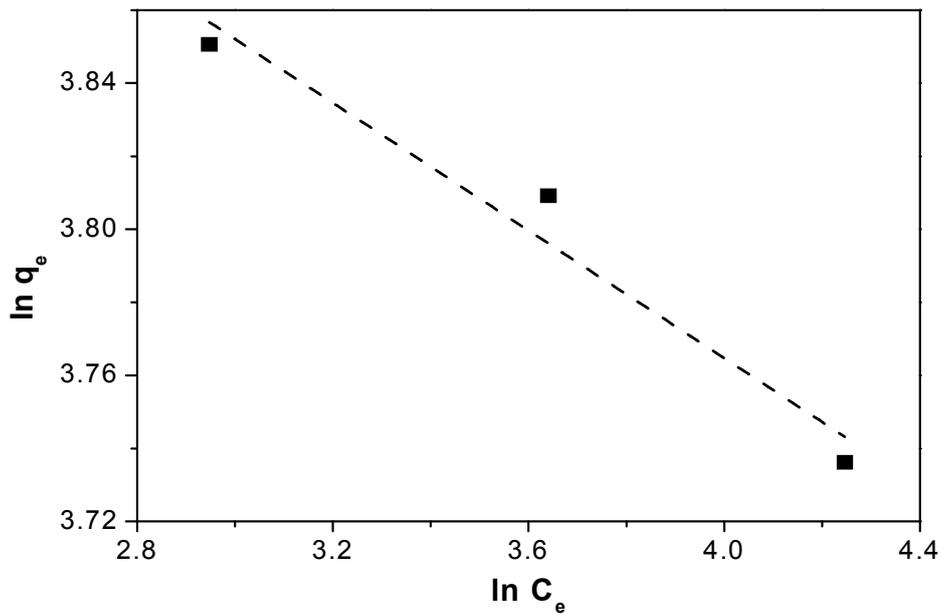


Fig. 7: Freundlich isotherm for adsorbate  $Cu^{+2}$  and adsorbent (AMBEREP 252H).

The Freundlich adsorption equation as in (8):

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \text{ -----(8)}$$

where  $K_f$  and  $n$  represent the adsorption capacity and intensity, respectively.  $K_f$  is an important constant used as relative measure for adsorption efficiency. The magnitude of the  $n$  shows an indication of the favorability of adsorption. Value of  $n$  is larger than 1 and show the favorable nature of adsorption as in Ref. (Daneshvar *et al.*,

2002 ).  $\ln q_e$  plotted versus  $\ln C_e$  and presented in (Fig. 7). This figure reveals the data for adsorption of  $\text{Cu}^{+2}$  ions onto AMBERSEP 252H resin fitted to the Freundlich adsorption isotherm.

C- Temkin Isotherm

The linear form equation for Temkin adsorption isotherm is expressed as in eq. (9) :

$$q_e = (RT/b_T) \ln A_T + (RT/b_T) \ln C_e \quad \text{----- (9)}$$

where:

$$B_T = RT/b_T \quad \text{----- (10)}$$

Where  $A_T$  (L/g) and  $b_T$  (J/mol) is Temkin constant representing adsorbate-adsorbent interactions and R is the gas constant (8.314 j/mol K), T is the absolute temperature.  $b_T$  is constant related to adsorption heat (Tan *et al.*, 2007).

Temkin isotherm takes into account the adsorbing species adsorbent interactions. Isotherm constants  $A_T$  and  $B_T$  can be determined from the plot of  $q_e$  versus  $\ln C_e$  as shown in (Fig. 8). According to Table (3) the value of  $A_T$  means in cation exchange processes by using AMBERSEP 252H, adsorbate/adsorbent interactions effective for copper ( $\text{Cu}^{+2}$ ) ions. All constants determined from Langmuir, Freundlich and Temkin isotherms are given in Table 3.

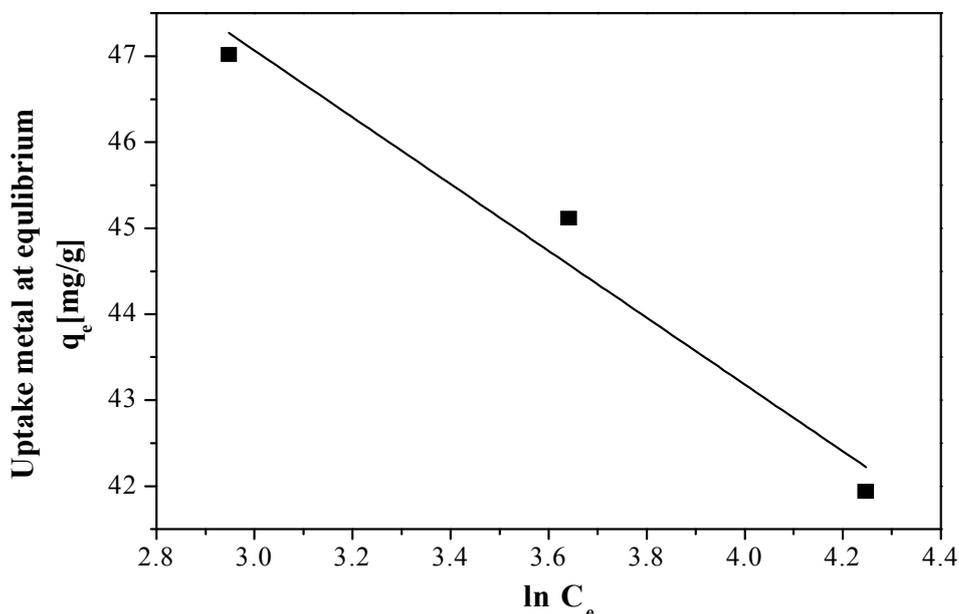


Fig. 8: Temkin model for adsorption of Copper ions (adsorbate) on the surface of AMBERSEP 252H (Adsorbent).

Table 3: Isotherm constants of adsorption isotherm models.

Langmuir isotherm		Freudlich isotherm		Temkin isotherm		(D-R) isotherm	
$V_m$	$K$	$n$	$K_f$	$B_T$	$A_T$	$-\beta$	$X_m$
40.12841	-0.0021	11.444	61.2	-3.88	$2.2 \times 10^{-7}$	$6.8 \times 10^{-6}$	41.74

D- Dubinin-Radushkevich (D-R) Adsorption Isotherm

The Dubinin-Radushkevich (D-R) isotherm ( Shin *et al.*, 2007) was also employed to find out the adsorption mechanism based on the potential theory assuming a heterogeneous surface. D-R isotherm equation form is expressed as follows (Eq.11) :

$$\ln q_e = \ln X_m - \beta \mathcal{E}^2 \quad \text{----- (11)}$$

Where  $X_m$  is the Dubinin-Radushkevich monolayer capacity (mg/g),  $\beta$  is a constant related to adsorption energy, and  $\mathcal{E}$  is the Polanyi potential ( Bulut and Tez, 2007) which is related to the equilibrium concentration as follows (Eq. 12):

$$\epsilon = RT \ln(1 + 1/C_e) \text{ -----(12)}$$

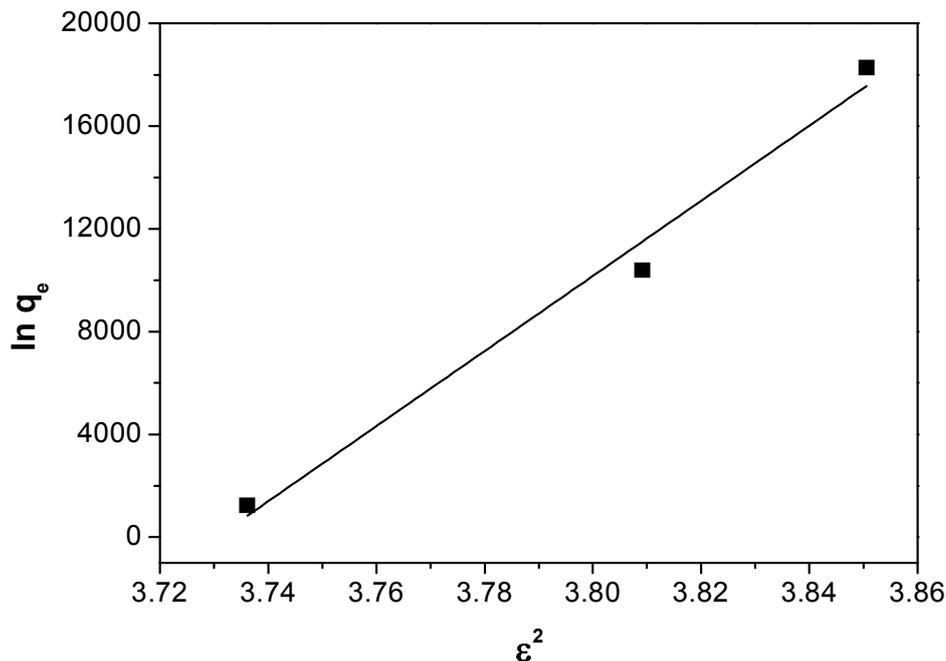


Fig. 9: D-R isotherm model for adsorption of Cu<sup>+2</sup> ion on the surface of resin.

A plot of  $\ln q_e$  vs.  $\epsilon^2$  in ( Fig. 9 ) gave a straight line from slope and intercept the values of  $\beta$  and  $X_m$  can be evaluated. The difference in the free energy between the adsorbed phase and the saturated liquid adsorbate is referred to as the Polanyi potential developed by Dubinin and his co-workers (Bulut *et al.*, 2007 and Shin *et al.*, 2007).

Thus the adsorption space in the vicinity of the solid surface may be characterized by a series of equipotential surfaces with a given adsorption potential. The adsorption potential is dependent of temperature but varies according to the nature of the adsorbent and adsorbate. ( $X_m$ ) and ( $\beta$ ) are tabulated in Table 3 .

The magnitude of  $\beta$  is used to determine the type of adsorption mechanism. When one mole of ions is transferred into the adsorbent surface, its value is higher than 8.0 kJ/mol which indicates a chemical adsorption was occurred.

**Conclusions**

The removal of Cu<sup>+2</sup> ions from aqueous medium using AMBERSEP 252H resin with different concentration of Cu<sup>+2</sup> ions and temperatures was investigated. Besides, the adsorption process of Cu<sup>+2</sup> ions onto AMBERSEP 252H resin in presence of acid medium and different temperatures was tested. Percentages of removal copper ions using such resin at different temperatures (write the temperature values) were 93.5%, 96.8% and 98.7%, respectively. On the other hand, the adsorption of metal ions was higher at low HCl concentration than for higher ones. Langmuir isotherm model was highest correlation coefficient in the adsorption process. Detailed studies will be needed for further evaluation of ion exchange resin (AMBERSEP 252H ) in the water treatment to remove chemical pollutant which obtained from the chemical industry.

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