



## Original Research Article

### Removal of toxic copper ions using alumina

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#### ABSTRACT

##### Keywords

Adsorption,  
Toxic  
copper,  
Langmuir  
model,  
Alumina.

In this work alumina was used as a non-conventional, coast-effective sorbent for removal of Cu (II) from aqueous solutions in batch systems. The sorbent was characterized with respect to surface area, pore volume, density, etc. the equilibrium sorption data were applied to various sorption isotherm models, as Langmuir, Freundlich and Dubinin-Kaganer-Radushkevich (D-R) adsorption isotherm. The kinetic uptake data were best interpreted by a pseudo second –order kinetic model with values of rate constants of adsorption of  $1 \times 10^{-3} - 15 \times 10^{-2}$  g/mg.min, respectively, for initial sorbate concentrations of 50 and 300 mg.l<sup>-1</sup> at 27°C. The sorption mean free energy was determined from the Dubinin-Kaganer-Radushkevich (D-R) isotherm model and was found to be below 8kJ/mol, indicating reaction mechanism gives through physical adsorption. The Cu (II) uptake was found to increase with the pH of the sorbate solution and maximum sorption was observed in the sorbate solution and maximum sorption was observed in the pH range.

#### Introduction

Removal of toxic heavy metals such as copper, lead, mercury, cadmium, chromium and arsenic from various wastewater is considered as one of the most important and challenging areas of water treatments. The rapid and growing industrialization have led to excessive disposal of heavy metals creating major environmental pollution problems and global concern Li, et al., 2009). Moreover, heavy metals are often detected in wastewaters as a result of industrial activities Quintelas et al., 2009).

Heavy metals are known for their non-biodegradability and accumulation in living systems, causing serious diseases and disorders. Various methods of heavy metals removal from wastewaters have been the subject of different researches (Bhattacharya et al., 2006). Most of these processes are unacceptable owing to their high cost, low efficiency, disposal of sludge, inapplicability to a wide range of pollutants (Quintelas et al., 2009). Adsorption, on the other hand, is one of the most recommended physico-chemical

treatment processes that is commonly used and applied for heavy metals removal from water samples and aqueous solutions. In addition, adsorption process is well recognized as one of the most efficient methods for removal of heavy metals from their matrices. Adsorption is mainly based on the utilization of solid adsorbents from organic, inorganic, biological or low cost materials (Jal et al., 2004).

Heavy metal removal via adsorption by organic adsorbents is usually accomplished by the applications of polymeric ion-exchangers in which the binding and interaction of metal species with these adsorbents is favored via ion-exchange mechanism or by applications of chelating polymers where as the target metal ions are directly attached to this kind of adsorbents via chelation or complex formation mechanism (Mahmoud et al., 1997).

The adsorption has many advantage such as: low cost of adsorbents, easy availability, utilization of industrial, biological and domestic waste as adsorbents, low operational cost, ease of operation compared to other process reused of adsorbent after regeneration, capacity of removing heavy metals ions over wide range of pH and to much lower level, ability to remove complex from metals that is generally not possibly by other methods, environmentally friendly, cost effective and technically feasible alternative due to utilization of biomaterials.

Copper is one of major contaminants released from metal finishing, electroplating and electrical industries. In humans, copper toxicity causes itching and dramatization and keratinization of the hands and soles of feet (Huang Yh, 2006).

Severe gastro-intestinal irritation and possible changes in the liver and kidneys occur due to intake of large doses of copper (Ajmal, et al., 1998).

Inhalation of copper spray increases the risk of lung cancer among exposed workers (Aydin, et al., 2008). According to the world health organization (WHO) and United States Environmental Protection Agency (USEPA), the maximum permissible limit of copper drinking water is  $1.3 \text{ mg l}^{-1}$  (Hach Company, 2003). Hence the removal of copper from wastewater before its discharge into aquatic systems is extremely important and deserves immediate attention.

Out of various methods employed for the removal of Cu (II) from aqueous solution adsorption appears to be the most frequently adopted technique (Bajpai Sk and Rohit, 2007). Addition, continuous attempts have been made to develop low cost non-conventional adsorbents for removal of toxic metal ions including Cu (II).

Inorganic solid adsorbents as alumina, silica and zirconia are well characterized by their high mechanical properties and strong resistivity to thermal degradation as compared to other biosorbents. In addition, several other advantages of alumina are characterized when used and applied as adsorbent for heavy metals removal and these include high surface area, existence in several structures and amphoteric properties (Dadfarnia, and Jafarzadeh, 1999). Activated form of alumina is also considered as one of the most commonly used adsorbent for heavy metals removal.

**Table.I** Properties of Activated alumina (Grade AD. 101)

Properties	Quantitative value
Surface area (cm <sup>2</sup> g <sup>-1</sup> )	370
Particle size (spherical mm)	2.0 ± 0.1
Pore volume (ml g <sup>-1</sup> )	0.42
Bulk density (kg m <sup>-3</sup> )	800
Loss on attrition (%)	0.2
Al <sub>2</sub> O <sub>3</sub> (%)	93.1
Na <sub>2</sub> O (%)	0.02
Fe <sub>2</sub> O <sub>3</sub> (%)	0.04
SiO <sub>2</sub> (%)	0.03

The metal ions are not only removed by adsorption on the surface of alumina but also by surface attraction/chemical bonding interaction (Dadfarnia, and Jafarzadeh, 1999).

## Experimental Work

### Experimental Work for Adsorption

#### Methods

All chemical used in this work were analytical reagent as laboratory reagent grade and were used as CuSO<sub>4</sub> supplied by BDH chemical limited distilled water were used.

#### Effect of initial concentration

Dilute 1000 mg/l of Cu<sup>2+</sup> to 50, 100, 150, 200 and 300 mg/l. Add 01 gm adsorbent (activated alumina (Grade Ad.101)) to 100 ml Cu<sup>2+</sup> aqueous solutions with the previously prepared concentrations. The mixture was for one hour, 1 ml of sample was taken from the reaction solution after 0, 5, 10, 15, 20, 30, 45 and 60 minutes and diluted to 10 ml with deionized water, the solution is then separated from the

adsorbent by using Whatman filter paper No.1. Repeat this experiment using 0.3, 0.5, 0.7 and 1.0 gm activated alumina.

#### Effect of pH

Dilute 1000 mg/l Cu<sup>2+</sup> to 100 mg/l. Add 0.5 gm adsorbent (alumina) to 100 ml Cu<sup>2+</sup> aqueous solution. Adjust the pH to 3, 5, 6, 8 and 9 by adding 0.1 N H<sub>2</sub>SO<sub>4</sub> or 0.1 N strong NaOH. The mixture was for one hour, 1 ml of sample was taken from the reaction solution after 0, 5, 10, 15, 20, 30, 45 and 60 minutes and diluted to 10 ml with deionized water, the solution is then separated from the adsorbent by using Whatman filter paper No.1.

## Results and Discussion

Analysis of adsorption data is important for developing equilibrium and kinetic equations that can be used for design purpose.

#### Effect of pH on the uptake of Cu<sup>2+</sup>

pH is an important parameter influencing heavy metal adsorption from aqueous solutions. The effect of pH on the adsorption capacity of Cu<sup>2+</sup> with alumina has been examined. The pH ranging between 3 and 8 is shown in Fig.(1). The experiment of adsorption as a function of pH was conducted at known initial concentration of 100 mg/l Cu<sup>2+</sup>, 0.5 g of alumina at 25°C.

The results reveal that increases from 3 to 6, the % removal increase to 78.4 % and adsorption capacity increases, this is because decrease of removal of metal ion at low pH due to the higher concentration of H<sup>+</sup> ion in the solution which compete with Cu<sup>2+</sup> for the adsorption site of adsorbents. Generally the positive charges

of adsorbent surface decreases with increasing pH to value 6 leading to the decrease in the repulsion between adsorbent and  $\text{Cu}^{2+}$ , thus improving the adsorption capacity (Antunes, et al., 2003)

Fig.1 Shows the effect of pH on adsorption capacity of the used adsorbents towards  $\text{Cu}^{2+}$ , the adsorption capacity increases by increasing pH from 3 to 8. The surface functional group gets negatively charged so attraction between the surface functional group and metal ion increases.

In contrast at higher pH value than 6 the % removal and adsorption capacity decrease due to metal precipitation (as metal hydroxides precipitate) appeared and adsorbent was deteriorated with accumulation of metal ions. Therefore pH 6 was selected to be optimum pH for further studies (Rudzinski, W. Plazinski, 2009).

#### **Effect of initial metal ion concentration**

The effect of the initial metal ion concentration on adsorption capacity of alumina was carried out at a contact time (60 min), pH 5.8 and temperature 298 K for different initial metal ion concentrations (50 ,100,150,200 and 300 mg/l) is shown in Fig.2.

Fig.(2) and Table (1) show that the quantity adsorbed of  $\text{Cu}^{2+}$ ,  $q_e$ , (mg/g) increased with the increase in the initial ion concentrations (Rudzinski, W. Plazinski, 2009; Azizian , 2004).

Furthermore, the results presented in Fig.(3) and Table (1), shows that the removal percentage of the adsorbed  $\text{Cu}^{2+}$  ions decrease with the increase of the

initial concentration. This decrease in copper removal percentage could be due to lack of sufficient active sites on alumina to adsorb more metal ions available in the solution (Sing, et al., 2012) (i.e. saturation of alumina sites at higher concentrations of copper ions). So, the percentage removal depended upon the initial metal ions concentration. This indicates the possible mono layer formation of metal ions on the outer surface of alumina

#### **Effect of adsorption dose**

The effect of adsorbent dose on the adsorption process was studied at a contact time 60 minutes for initial  $\text{Cu}^{2+}$  concentration 50, 100, 150, 200 and 300 mg/l at 25°C. The amount of adsorbent varied from 0.1 to 1 gm.

In Fig.5 an increase in the removal percentage is noted as the amount of adsorbent used increases. That is expected, because at a fixed initial concentration of sorbate the increase in the adsorbent amount provides a larger surface area or adsorptive sites. However according to Fig.5, the adsorbed amount per unit mass of adsorbent ( $q_e$ ) declines. The decrease in adsorbed amount per unit mass of adsorbent is a generally observed behavior. It has also reported by the many researchers (Gupta, and Bhattacharyya, 2008). This may be attributed to two reasons:

(i) A large adsorbent amount effectively reduces the instauration of the adsorption sites and correspondingly, the number of such sites per unit mass comes down resulting in comparatively less adsorption at higher adsorbent amount, and

ii) Higher adsorbent amount creates

particle aggregation, resulting in a decrease in the total surface area and an increase in diffusional path length both of which contribute to decrease in amount adsorbed per unit mass (Sing, et al., 2012)

### **Effect of contact time**

The effect of contact time was studied, while all other variables such as adsorbent dosage, pH and volume of solution, temperature and rotation speed are kept constant. This method is known as optimization which are based on one factor at a time where one parameter is varied, and the others are kept constant.

The variation in adsorption capacity ( $q_t$ ) with time is studied using solutions of initial concentrations of (50,100, 150, 200, 300 mg/l) at pH 5.8. The results are given in Fig.(5). It is revealed that  $Cu^{2+}$  uptake was very rapid during the first five minutes. After five minutes,  $Cu^{2+}$  adsorption rates slowly declined and reach equilibrium at 60 minutes. From Fig. (5), it can be seen that the percentage of metal ion adsorption increased with increasing time. The removal of  $Cu^{2+}$  increased with time to obtain equilibrium at about 60 minutes.

Very high adsorption rates were observed at the beginning because of the great number of sites available for the sorption operation and adsorption equilibrium were then gradually achieved (Onal, et al., 2007; Fiol, et al., 2006).

The removal of  $Cu^{2+}$  occurred in two steps: (Onal, et al., 2007)

- (i) a first step in which the removal increased rapidly (about 30 minutes)
- (ii) a slower second phase in which the removal increased slowly (from about 30

minutes until the end of the experimental period).

The fast step is probably due to the abundant availability of active sites on the adsorbent, and with the gradual occupancy of these sites, the sorption becomes less efficient in the slower step (Fiol, et al., 2006)

### **Lagergen pseudo first order kinetic model**

The pseudo first order equation is probably the earliest known example describing the rate of adsorption in the liquid-phase systems. This Eq. (1) has been one of the most used equations particularly for pseudo first order kinetics:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t)$$

(1)

Where  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo first order adsorption rate coefficient. The integrated form of the Eq. (1) for the boundary conditions of  $t=0, q_t = 0$  and  $t=t,$

$$q_t = q_e,$$

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

(2)

Where  $q_e$  and  $q_t$  are the values of amount adsorbed per unit mass at equilibrium and at any time  $t$ . The values of  $k_1$  can be obtained from the slope of the linear plot of  $\ln (q_e - q_t)$  vs.  $t$  as show in Fig. (6) and Table (2).

The value of  $k_1$  depends on the initial concentration of the adsorbate that varies from one system to another. It usually decreases with the increasing initial

adsorbate concentration in the bulk phase (Sing, et al., 2012; Gupta and Bhattacharyya, 2008).

The real test of the validity of Eq. (2) arises from a comparison of the experimentally determined  $q_e$  values (McKay et al., 1999; Ho et al., 1998) and those obtained from the plots of  $\ln (q_e - q_t)$  vs.  $t$ . If this test is not valid, then higher order kinetic models are to be tested with respect to the experimental results. A difference of equilibrium sorption capacity ( $q_e$ ) between the experimental and the calculated data was observed, indicating a poor pseudo first-order fit to the experimental data

### **Pseudo-second order kinetic model**

The second order kinetics model may be tested on the basis of the Eq. (3),

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (3)$$

Where  $k_2$  is the rate of pseudo second order adsorption. Separation of the variables followed by integration and application of the boundary conditions ( $q_t=0$  at  $t=0$  and  $q_t=q_t$  at  $t=t$ ) yields a linear expression of the form

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

$k_2$  often depends on the applied operating conditions, namely, initial metal concentration, pH of solution, temperature and rotation speed, etc. (Ho, et al., 1998; Plazinski, et al., 2009). The integral form of the model, represented by the Eq. (4) predicts that the ratio of the time/adsorbed amount ( $t/q_t$ ) should be a linear function of time (Ho et al., 2006).

Both theoretical investigations (Rudzinski, W. Plazinski, 2006; Ho, G. McKay, 1998) and the experimental studies indicate that the value of  $k_2$  usually depends on the initial adsorbate concentration in the bulk phase. The rate coefficient,  $k_2$ , decreases with the increasing initial adsorbate concentration as a rule, where  $k_2$  is explained as a time-scaling factor. Thus, higher is the initial concentration of adsorbate, the longer time is required to reach an equilibrium, in turn, the  $k_2$  value decreases (Al-Ghouti et al., 2009; Nandi, et al., 2009).

The pseudo-second order equation has also been explained as a special kind of Langmuir kinetics. This line of explanation assumes that:

- (i) The adsorbate concentration is constant in time and
- (ii) The total number of binding sites depends on the amount of adsorbate adsorbed at equilibrium.

One of the advantages of the pseudo-second order equation for estimating the  $q_e$  values is its small sensitivity for the influence of the random experimental errors.

The applicability of the above two models was examined by each linear plot, as presented in Fig. (7) and Table (2). To quantify the applicability of each model, the correlation coefficient,  $R^2$ , was calculated from these plots. The linearity of these plots indicated the applicability of the two models. The kinetic rate constants obtained from pseudo first and second order adsorption models are given in Tables (3.20). The values of  $R^2$  for the pseudo second order model is relatively

high (>0.995), and the adsorption capacities calculated by the model are also close to those determined experimentally. Therefore, it has been concluded that the pseudo second order model is more suitable for describing the adsorption kinetics of copper on alumina

**Weber and Morris model**

The pseudo-first and second kinetic models cannot identify the diffusion mechanism, so the kinetic data are further analyzed using the intra-particle diffusion model proposed by Weber and Morris (189,190). The intra-particle diffusion equation can be written as follows:

$$q_t = k_{id}t^{1/2} + C \tag{5}$$

Where  $k_{id}$  is the intraparticle diffusion rate constant ( $mg\ g^{-1}\ min^{-1/2}$ ).

According to this model, when the intraparticle diffusion is involved in the adsorption process, the plot of  $q_t$  versus  $t^{1/2}$  gives a straight line with a slope  $k_{id}$  and an intercept  $C$ . The values of  $C$  provide an approximation of the boundary layer thickness, the greater the  $C$  value, the greater the boundary layer. If the lines of the plot pass through the origin, then the intraparticle diffusion is the rate determining step. As shown in Fig. (8), the intercepts of the lines do not pass through the origin indicating that the mechanism of  $Cu^{2+}$  adsorption on alumina is complex and involve two or more steps such as surface adsorption and intraparticle diffusion. The values of  $k_{id}$ ,  $C$  and  $R^2$  are given in Table (2).

**Isotherm models**

Analysis of equilibrium data is important to develop an equation which accurately

represents the results and which could be used for design purpose. Freundlich, Langmuir and D-R isotherm equations have been reported most frequently for the equilibrium modeling of adsorption systems.

**Langmuir adsorption isotherm**

The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption and there is no interaction between sorbed species. The Langmuir equation (6) is expressed as follows (32):

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot b} + \frac{C_e}{q_{max}} \tag{6}$$

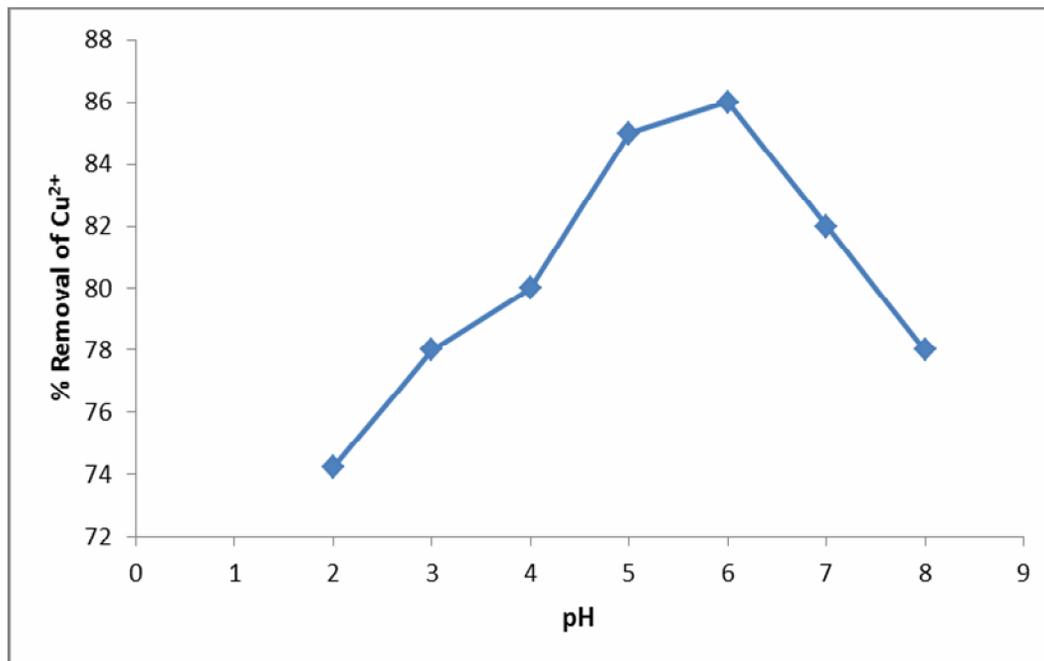
Where:  $q_e$  is the equilibrium metal ion concentration on the adsorbent (mg/g),  $C_e$  the equilibrium metal ion concentration in the solution,  $q_{max}$  the monolayer adsorption saturation capacity of the adsorbent and  $b$  is the Langmuir constant.

A plot of  $C_e/q_e$  versus  $C_e$  gives a straight line, and the values of a slope ( $1/q_{max}$ ) and an intercept ( $\frac{1}{q_{max} \cdot b}$ ) as shown in Fig.(9).

The linear plot shows that the adsorption verifies the Langmuir isotherm. The Langmuir adsorption constant and the regression correlation coefficient are given in Table (2).

The essential characteristics of the Langmuir can be expressed by dimensionless number constant, the separation factor or equilibrium

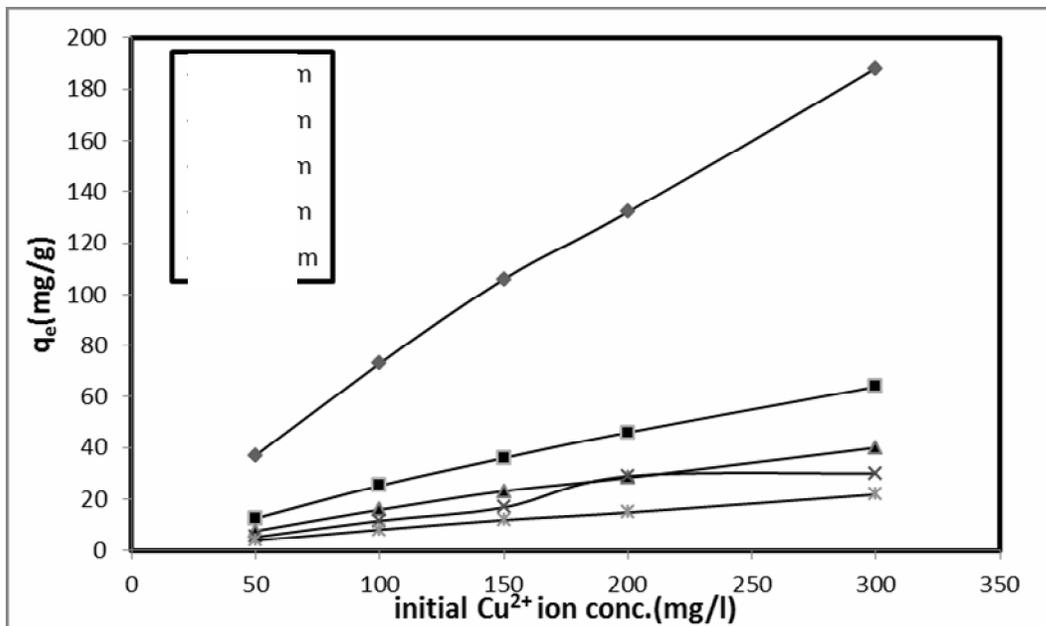
**Fig.1** Variation of % removal of  $\text{Cu}^{++}$  ions with pH at 100 ppm  $\text{Cu}^{++}$ , 0.5 g dose and 25°C.



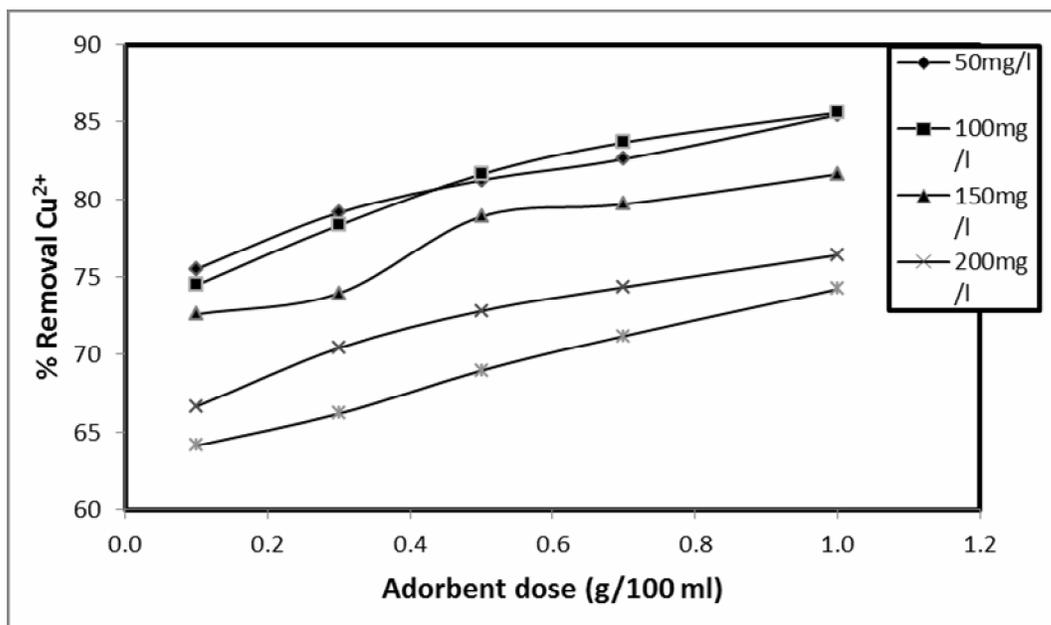
**Table.1** The effect of different initial  $\text{Cu}^{2+}$  ion concentrations on the quantity adsorbed of  $\text{Cu}^{2+}$ ,  $q_e$ , (mg/g) and % removal of  $\text{Cu}^{2+}$  for 100 ml solutions contain different concentrations of  $\text{Cu}^{2+}$  and different alumina doses (g/100 ml) at pH=5.8; contact time 1 h and at 25°C.

alumina dose (g/100 ml) $\text{Cu}^{2+}$ conc. (mg/l)	0.1	0.3	0.5	0.7	1.0
	$q_e$ , (mg/g)				
50	37.00	12.67	7.80	5.43	4.10
100	73.00	25.33	16.00	11.71	8.30
150	106.00	36.00	23.20	16.86	12.00
200	132.00	46.00	28.40	29.00	14.90
300	188.00	64.00	40.00	30.00	21.90
alumina dose (g/100 ml) $\text{Cu}^{2+}$ conc. (mg/l)	0.1	0.3	0.5	0.7	1.0
	% removal				
50	75.51	79.17	81.25	82.61	85.42
100	74.49	78.35	81.63	83.67	85.57
150	72.60	73.97	78.91	79.73	81.63
200	66.67	70.41	72.82	74.36	76.41
300	64.16	66.21	68.97	71.19	74.24

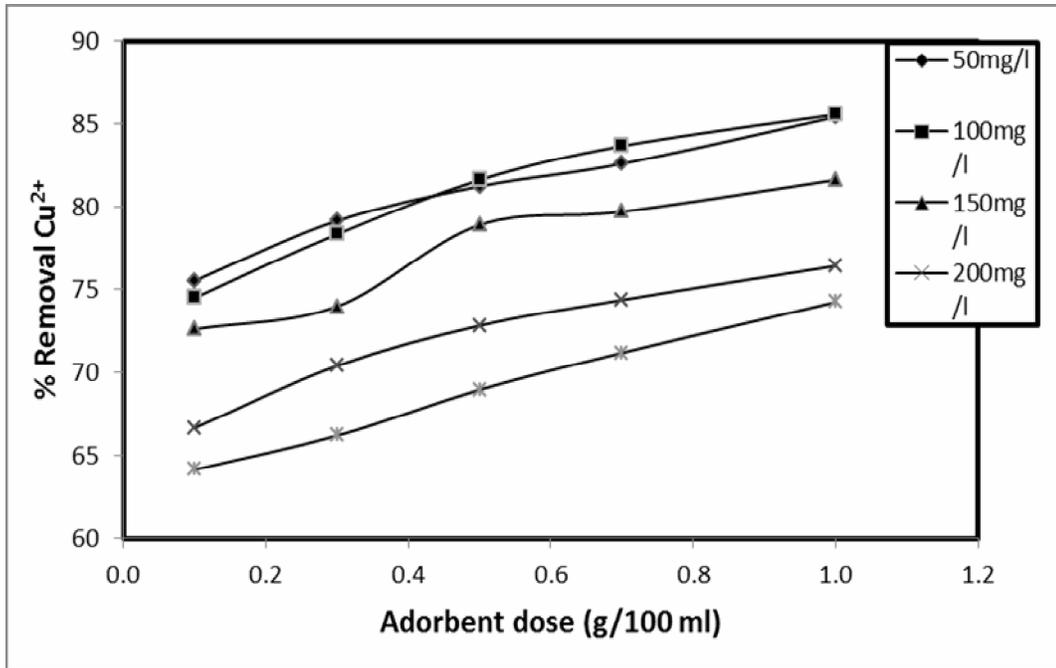
**Fig.2** Effect of initial  $\text{Cu}^{2+}$  ion concentration on the adsorption capacity of alumina,  $q_e$ , (mg/g) for 100 ml solutions contain different concentration of  $\text{Cu}^{2+}$  and different alumina dose (g/100 ml) at pH=5.8; contact time 1 h and at 25°C.



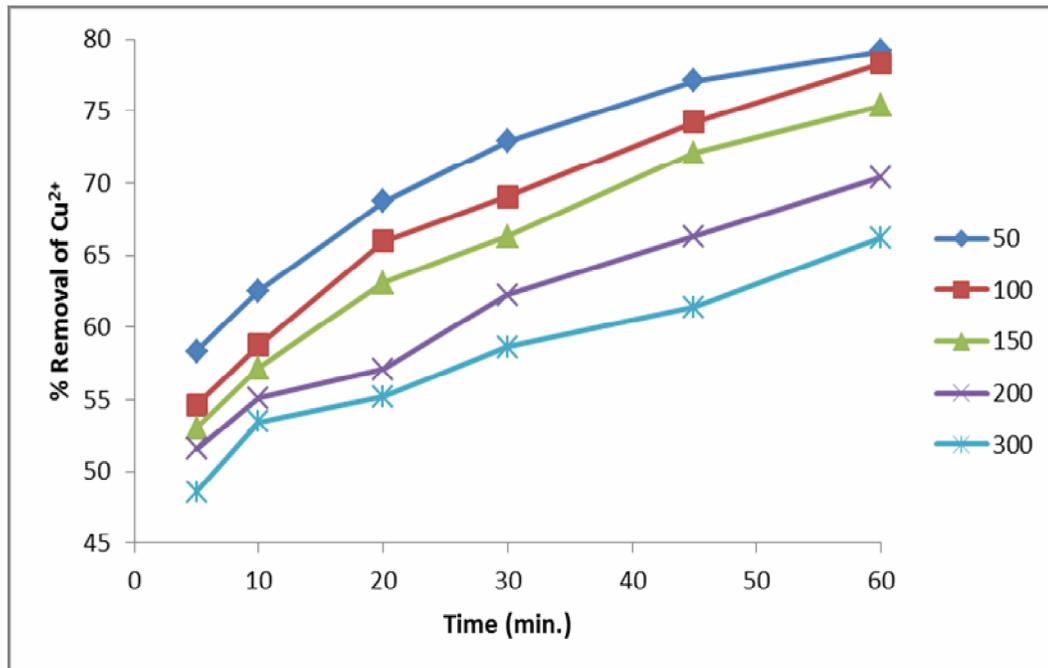
**Fig.3** Variation of % removal  $\text{Cu}^{2+}$  ions with the adsorbent dose of activated alumina at different initial concentrations of  $\text{Cu}^{2+}$  ions (mg/l) at 25°C; contact time 1 h and pH 5.8.



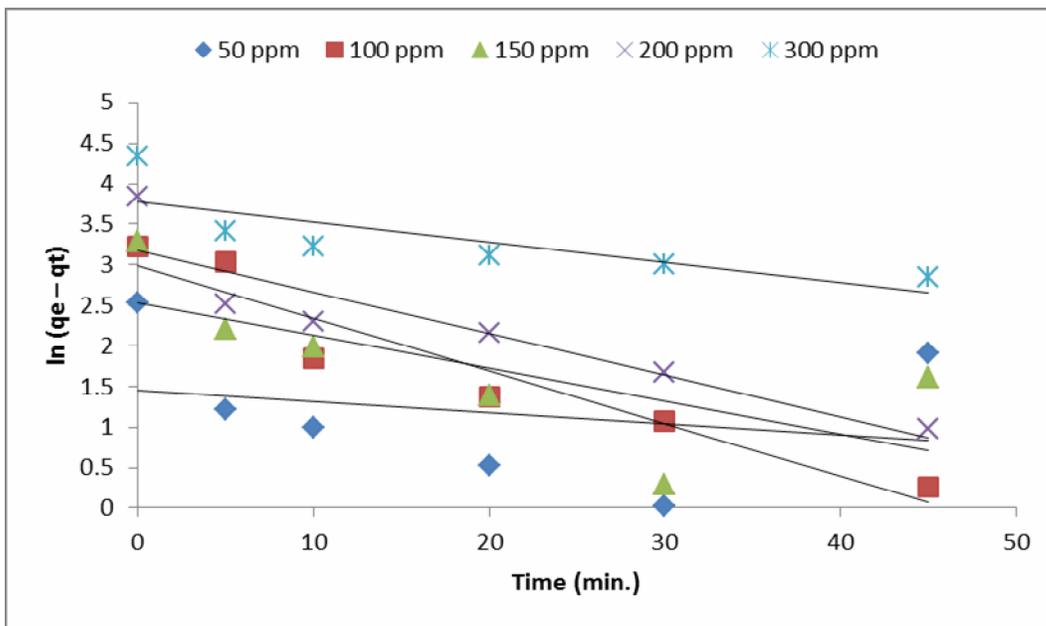
**Fig.4** Effect of alumina dose on adsorption capacity for different initial concentrations of  $\text{Cu}^{2+}$  ions (mg/l) at 25°C; contact time 1 h and pH 5.8.



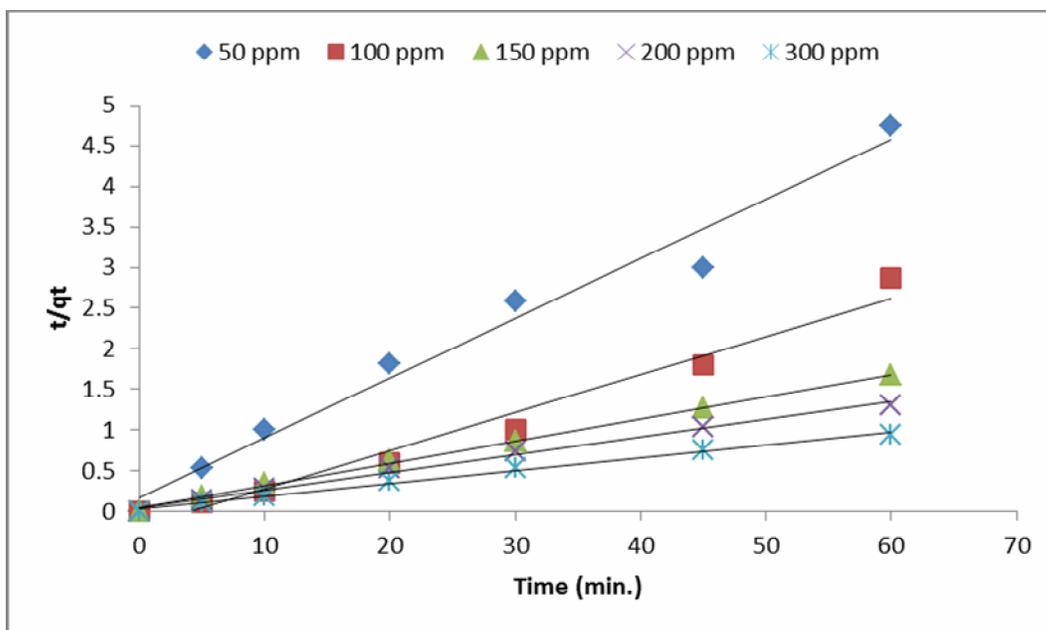
**Fig.5** Effect of contact time on % removal of  $\text{Cu}^{+2}$  in presence of 0.5g aluminum and 100 ppm at pH 5.8



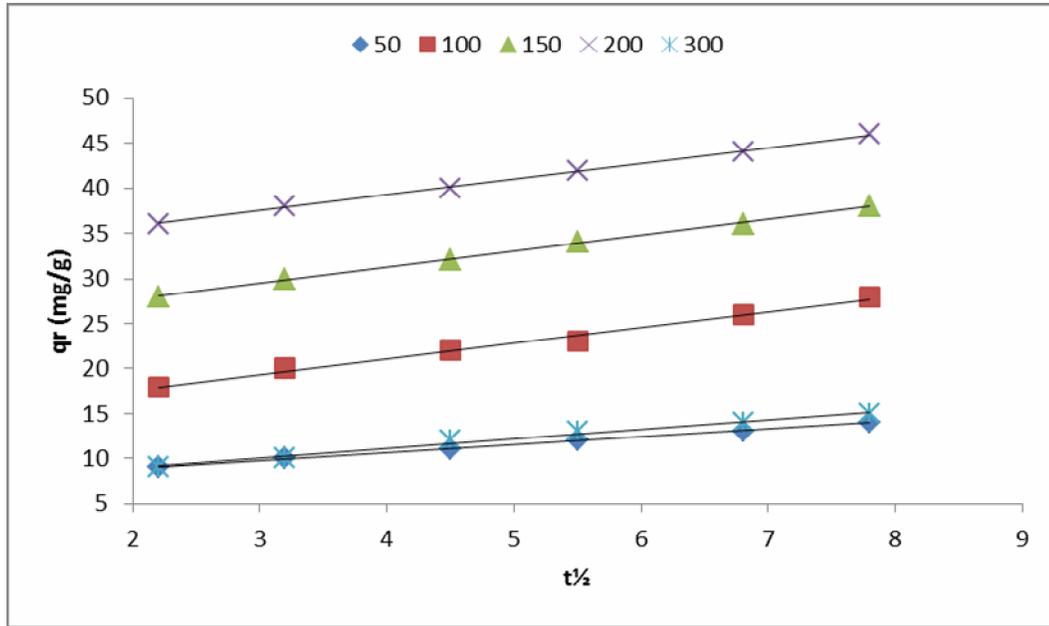
**Fig.6** Pseudo-first order kinetic plots for the adsorption of different initial concentrations of  $\text{Cu}^{2+}$  ions 100 mg/l using different alumina doses (g/100 ml) at 25 °C; contact time 1 h and pH 5.8.



**Fig.7** Pseudo-second order kinetic plots for the adsorption of different initial concentrations of  $\text{Cu}^{2+}$  ions and using different alumina doses (g/100 ml) at 25°C; contact time 1 h and pH 5.8.



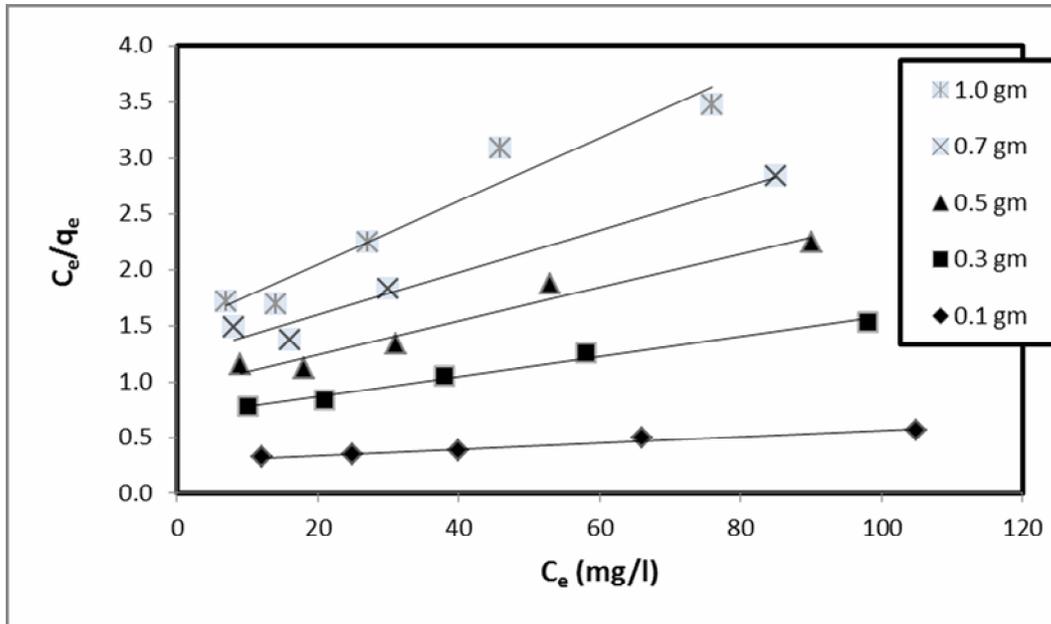
**Fig.8** The intra-partial diffusion model for adsorption of different initial concentration of  $\text{Cu}^{+2}$  ion at 25°, 0.3g alumina, pH = 5.8 and contact time 1 h.



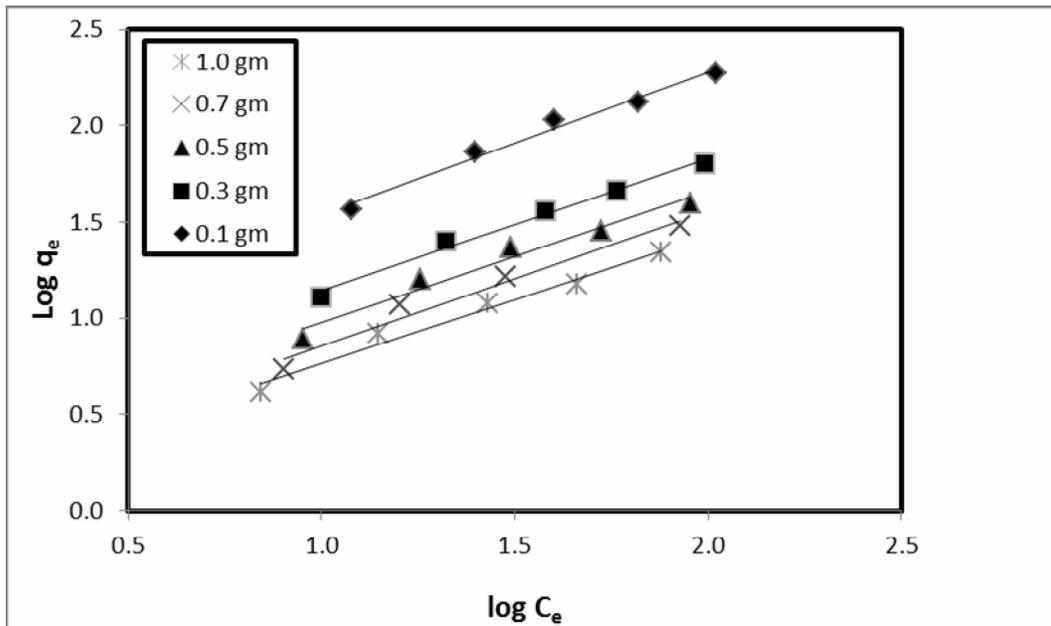
**Table.2** The adsorption kinetic data for 100 ml solution contain different concentration of  $\text{Cu}^{2+}$  in presence of different alumina dose at contact time 1 h, various ppm and pH 5.8.

Kinetic models	Conc.	50 ppm	100 ppm	150 ppm	200 ppm	300 ppm
	Parameters					
Pseudo-first order equation	$q_e(\text{Exp})$ (mg/g)	12.67	25.33	36.00	46.00	64.00
	$q_e$ (Calc.) (mg/g)	7.32	14.3	20.09	24.05	44.26
	$k_1(\text{min}^{-1})$	0.07	0.06	0.08	0.05	0.03
	$R^2$	0.83	0.89	0.93	0.88	0.84
Pseudo- second order equation	$q_e$ (Calc.) (mg/g)	12.82	27.03	33.33	46.3	66.67
	$k_2$ (g/mg. min)	0.04	0.009	0.018	0.009	0.004
	$R^2$	0.997	0.996	0.998	0.993	0.995
Intraparticle diffusion model	$k_{id}(\text{mg g}^{-1} \text{min}^{-1/2})$	0.62	1.36	1.73	2.21	3.56
	C	8.08	14.7	23.7	28.5	40.00
	$R^2$	0.98	0.99	0.94	0.98	0.956

**Fig.9** Langmuir adsorption isotherm for  $\text{Cu}^{2+}$  ions adsorption with different dose of alumina (g/100 ml) at 25°C; pH: 5.8 and contact time 1 h.



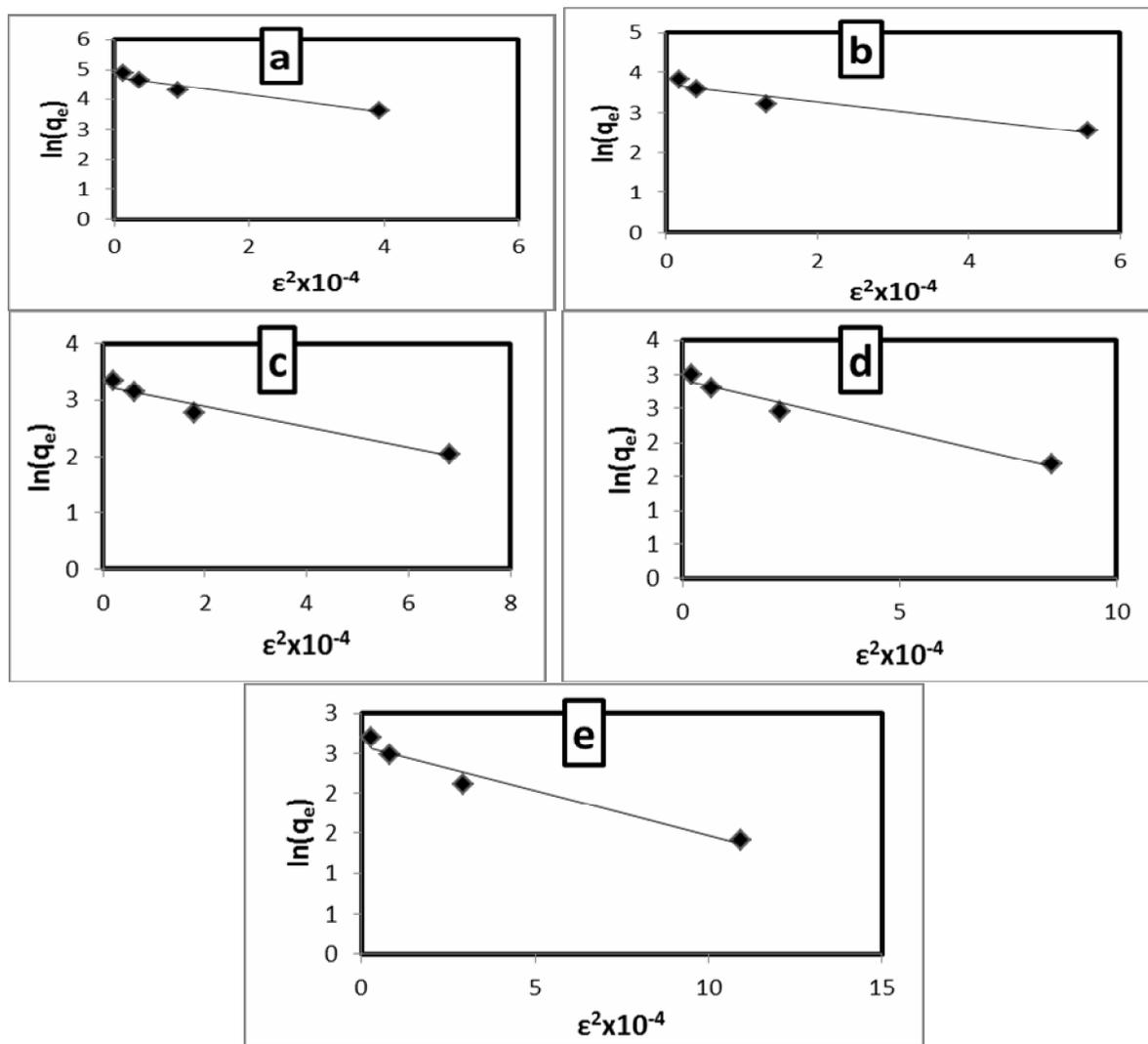
**Fig.10** Freundlich adsorption isotherm for  $\text{Cu}^{2+}$  ions adsorption onto different alumina dose (g/100 ml) at 25°C; pH: 5.8 and contact time 1 h.



**Table.2** Langmuir, Freundlich isotherm and D-R adsorption isotherm constants for the adsorption of Cu<sup>2+</sup> ions onto different doses of alumina at 25°C

Alumina dose (g/100 ml)	Langmuir Isotherm constants			Freundlich Isotherm constants			Dubinin–Radushkevich constants			
	q <sub>max</sub> (mg/g)	b (L/mol)	R <sup>2</sup>	$\frac{1}{n}$	K <sub>F</sub> (mg/g)	R <sup>2</sup>	-β (mol <sup>2</sup> /kJ <sup>2</sup> x10 <sup>5</sup> )	E (kJ/mol)	q <sub>max</sub> (mg/g)	R <sup>2</sup>
0.1	333.33	0.011	0.957	0.731	0.812	0.984	3	0.13	118.39	0.930
0.3	111.11	0.013	0.982	0.691	0.449	0.988	2	0.16	40.24	0.931
0.5	66.67	0.016	0.962	0.682	0.295	0.967	2	0.16	26.05	0.959
0.7	52.63	0.016	0.971	0.701	0.156	0.967	1	0.22	18.48	0.969
1.0	35.71	0.019	0.940	0.665	0.098	0.975	1	0.22	13.42	0.950

**Fig.11** The D-R adsorption for Cu<sup>2+</sup> ions adsorption onto different doses of alumina: a) 0.1 gm, b) 0.3 gm, c) 0.5 gm, d) 0.7 gm and e) 1.0 gm at 25°C; pH: 5.8 and contact time 1 h.



parameter ( $R_L$  given by Eq. (7):

$$R_L = \frac{1}{1 + bC_e} \tag{7}$$

The parameter  $R_L$  indicates the curvature of the sorption isotherm as follows:

$R_L$ Value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

From this study  $R_L$  values ranged from 0.34 to 0.47. Therefore the copper sorption in to alumina is considered favorable

### 3.10. Freundlich adsorption isotherm

The Freundlich adsorption isotherm, one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentrations. This isotherm gives an expression encompassing surface heterogeneity and the exponential distribution of active sites and their energies. The nonlinear form of Freundlich model is expressed as (Freundlich, et al., 1906):

$$q_e = K_F(C_e)^{1/n} \tag{8}$$

The linear form of Freundlich model is

expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{9}$$

Where:

$K_F$  is Freundlich constant representing the adsorption capacity and  $n$  is a constant related to the sorption intensity, which varies with the heterogeneity of the adsorbents.

A plot of  $\log q_e$  versus  $\log C_e$  gives a straight line with a slope  $(1/n)$  and an intercept  $(\log K_F)$  as shown in Fig.(10). The values of  $K_F$  and  $1/n$  are collected in Table (2). The value of  $1/n$  less than 1 represent of favorable sorption and confirmed the heterogeneity of the adsorbent. Also, it indicates that the bond between heavy metal ions and alumina are strong .

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

The D-R adsorption isotherm equation is more general than the Langmuir isotherm because it does not assume a homogenous surface or constant adsorption potential. It is applied to distinguish between physical and chemical adsorption. The linear form of D-R isotherm equation (10) is (Horsfall, andn Spiff, 2005):

$$\ln q_e = \ln q_{max} - \beta \epsilon^2 \tag{10}$$

Where:

$q_{max}$  (mg/g) is the maximum sorption capacity ,

$\beta$  ( $\text{mol}^2/\text{J}^2$ ) is a constant related to the mean free energy of adsorption per mole of the adsorbate

$\epsilon$  is the Polanyi potential, which is equal to (Riaz, et al., 2006):

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (11)$$

Where R is the gas constant (J/ (mol. K)) and T is temperature ( $^{\circ}$ K). Hence by plotting  $\ln q_e$  versus  $\epsilon^2$ , as shown in Fig. (11) and Table (2), it is possible to generate the value of  $q_{\max}$  from the intercept and the value  $\beta$  from the slope, as shown in Table (2).

The adsorption energy can also be worked out using the following relationship:

$$E = \frac{1}{\sqrt{2\beta}} \quad (12)$$

It is known that the magnitude of apparent adsorption energy E is useful for estimating the type of adsorption. If the value of E is below 8 KJ/mol the adsorption type can be explained by physical adsorption, between 8 and 16 KJ/mol the adsorption type can be explained by ion exchange, and over 16 kJ/mol the adsorption type can be explained by a stronger chemical adsorption than ion exchange (Atanassova, M. Okasaki .

The values of the adsorption energy (kJ/mol) are listed in Table (3.24). As shown, the values of the adsorption energy lie below 8 kJ/mol, and then reaction mechanism goes through physical adsorption

## References

Ajmal, M. H. Khan, S. Ahmed and A. Ahmed, *Water Res.*, 32, 3085 1998.  
 Aksu, Z. J. *Process Biochemistry*, 40, 997 2005.

Al-Ghouti, M.A M.A.M Khraisheh. M.N.M. Ahmad, S. Allen, J. Hazard Mater, 165,589 2009.  
 Antunes, W.M. A.S. Luna, C.A. Heniques, A.C. Costa, *Electronic Journal of Biotechnology ISSN*, 6, 174 2003.  
 Atanassova, I. M. Okasaki, *Water Air Soil Poll.*, 98, 2131997.  
 Aydin, Y H.. Bulut and C. Yerlikaya, J. *Environ. Manage.*, 87, 1, 37 2008.  
 Azizian , S. J. *Colloid Interface Sei.*, 276,47 2004.  
 Bajpai Sk and Rohit Vk, *EJEAF Chem.*, 6, 2053 2007.  
 Bhattacharya, A.K. S.N. Mandal, S.K. Das, *Chem. Eng. J.*, 123, 43 2006.  
 Dadfarnia, S. M.H. Jafarzadeh, *Microchem. J.*, 63, 226 1999.  
 Fiol, N .I. Villaescusa, M. Martinez, N. Miralles , J. Poch , J. Serarols. *Sep. Purif. Technol.*, 50,132 2006.  
 Freundlich, H. Concerning adsorption in solutions, *Z. Phys. Chem.*, 57, 385 1906.  
 Gupta, S.S. K.G. Bhattacharyya, J. *Environ. Manage.*, 87, 46 2008.  
 Hach Company 2003 *Hach Water Analysis Handbook 4<sup>th</sup> edn. Revision 2.* Hach Company, Loveland. 70 pp.  
 Hall, K.R. L.C. Eagleton, A. Acrivos, T. Vermeule, *Ind. Eng. Chem. Fundam.*, 5, 212 1966.  
 Ho, Y.S. G .McKay, *Ads. Sei. Technol.*,16,243 1998.  
 Ho, Y.S. G .McKay, *Trans. I. Chem. ,* 3,32 1998.  
 Ho, Y.S. G .McKay, *Water Res.*, 34,735 2000.  
 Horsfall, A M.J.. Spiff, *Acta. Chim. Slov.*, 52, 174 2005.  
 Huang Yh, Hsueh Cl, Cheng Hp, Su Lc and Chen Cy, *J. Hazard Mater.* 144, 406 2007.  
 Jal, P.K. S. Patel, B.K. Mishra, *Talanta*, 62, 1005 2004.  
 Kim, Y. C. Kim, I. Choi, S. Rengaraj, J.

- Yi, Environ. Sci. Technol., 38, 924 2004.
- Langmuir, I. J. Am. Chem. Soc., 40, 1361 1918.
- Li, Z., X. Chang, Z. Hu, X. Huang, X. Zou, Q. Wu, R. Nie, J. Hazard. Mater., 166,133 2009.
- Mahmoud, M.E. E.M. Soliman, A. El-Dissouky, Anal. Sci., 13, 765 1997.
- McKay, G .Y.S. Ho, J.C.Y. Ng , Sep. Purify. Methods, 28, 87 1999.
- Nandi, B.K. A. Goswami, M.K. Pnrkait., J. Hazard Mater., 161,387 2009.
- Onal S., S. Hamarat Baysal, G .Ozdemir, J. Hazard Mater, 146,417 2007.
- Plazinski, W. W. Rudzinski , A. Plazinska, Adv. Colloid Interface Sei., 2,152 2009.
- Quintelas, C.Z. Rocha, B. Silva, B. Fonseca, H. Figueiredo, T. Tavares, Chem. Eng. J., 149, 319 2009.
- Rengaraj, S. C.K. Joo, Y. Kim, J. Yi, J. Hazard. Mater., 102 , 257 2003.
- Riaz,; A. Y. Tayyab, M.S. Absari, S.M. Hasany, Adsorpt. Sci. Technol., 24, 475 2006.
- Rudzinski, W. W. Plazinski, Adsorption, 15,181 2009.
- Rudzinski, W. W. Plazinski, J. Phys. Chem., B101,6514 2006.
- Sing, L. A.R. Pavinkiemar, R. Lakshmanan , G.K. Rajaroo, Ecological Engineering, 38, 119 2012.
- Yu, B. Y. Zhang, A. Shukla. K..L. Dorris, J. Hazard. Mater. B 80, 33 2000.
- Zhang, Y. P. Riby, A.G. Cox, C.W. McLeod, A.R. Date, Y.Y. Cheung, Analyst, 113, 125 1988.