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# Elimination of Copper (II) Ions from Aqueous Solution by the using of gamma alumina nanoparticles

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## ABSTRACT

heavy metals, as gamma alumina nanoparticles pollutants, in water resources. Therefore, the purpose of this paper was to evaluate the removal of copper (II) ions from aqueous solutions using gamma alumina nanoparticles as a adsorbent. Batch adsorption studies carried out to study various parameters included contact time, initial concentration of copper (II) ions, pH, and gamma alumina nanoparticles dosage. The concentration of copper (II) ions was measured using a UV-vis Spectrophotometer at the wavelength of 390 nm. Freundlich and Langmuir isotherms were used to analyze the isotherm. Maximum adsorption took place at pH=6 for the gamma alumina nanoparticles adsorbent and the adsorption value was reduced with decrease of pH. It was found that Langmuir isotherm is well fitted with our data. According to Thermodynamic analysis, the process endothermic and natural ($\Delta H^o$= 94895.996 $J.mol^{-1}$and $\Delta S^o$= 320.230 $J.mol^{-1}K^{-1}$).

**Keywords:** copper (II) ions; Adsorption; Thermodynamic; gamma alumina nanoparticles

## INTRODUCTION

Transitional aluminas, particularly γ-alumina and θ-alumina, which are usually obtained by calcination of boehmite at different temperatures, are among the most important oxides used in the industrial applications. The gamma alumina are widely used as adsorbents, catalysts and catalysts supports, due to their large specific surface areas, well – defined pore size distributions, stability within a wide temperature range, ability to stabilize and disperse the active phases as well as moderate acidities. There are several reports representing key roles of gamma alumina as catalysts supports [1-3].

The removal of toxic metals from wastewater is of great interest in the field of water pollution, which is a serious cause of water degradation. Numerous metals such as chromium, mercury, lead, copper, cadmium, manganese, etc. are known to be significantly toxic. The presence of heavy metals in the environment can be detrimental to a variety of species. Therefore, the elimination of heavy metals from waters and wastewaters is important to protect public health. Heavy metals contamination of water and wastewater is a common phenomenon. The discharge of heavy metals into aquatic ecosystem has

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become a matter of concern over the last few decades. Industrial wastewaters are usually the cause of heavy metals pollution of the environment. These heavy metals find many applications in our life are very harmful if they discharged into natural water resources and pose a serious health hazard. Pollutants of serious concern include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, gold, copper and nickel. A number of materials have also been used to remove heavy metals from wastewater, such as activated carbon, silica, titanium dioxide, calcium carbonate, alumina, and recently, various nanomaterials such as nanometal oxides, carbon nanotubes, and nanozeolite composites [4-14]. This research focuses on the use of gamma alumina nanoparticles as a biosorbent for the removal of lead and copper ions from aqueous solution, was studied in batch equilibrium conditions. The effects of different parameters including pH, initial metal ion concentration, contact time, gamma alumina nanoparticles dosage and temperature were investigated. Langmuir and Freundlich isotherm models were used to analyze the equilibrium data.

## EXPERIMENTAL

### *Apparatus and Materials*

An AA 680 model atomic absorption spectrometer (Shimadzu Co.) was used to measure the concentration of copper (II) ions in the studied solutions, a 820 A model pH meter (Metrohm Co.) was used to measure pH of solutions and a thermostatic orbit incubator shaker neolab model (India) was used to measure contact time in the solutions. All chemical materials used in this study were of analytical grade.

### *Batch Adsorption Experiments*

Batch adsorption experiments were carried out to determine the copper (II) ions adsorption isotherm onto gamma alumina nanoparticles and its thermodynamic properties. copper (II) ions stock solution (100 mg.$L^{-1}$) was prepared by dissolving the appropriate quantity of copper (II) ions in deionized water. Adsorption isotherms were obtained by using initial copper (II) ions concentration, $M_o$, and its equilibrium concentration, $M_e$ at 298 K. The effect of pH on the copper (II) ions adsorption onto gamma alumina nanoparticles was evaluated in a pH range of 2-8. The pH of solutions was adjusted by 0.1 M HCl or 0.1 M NaOH solutions. For every experiment, 100 ml of the solution with copper (II) ions concentration of 10 mg.$L^{-1}$ was mixed with 50 mg of gamma alumina nanoparticles in a 250 ml glass conical flask which was shaken in a thermostatic orbit shaker at 220 rpm for 60 min. The mixture was filtered through a 0.45 μm membrane filter. The filtrate was measured by atomic absorption then, the adsorption percentage (%A) was determined as:

$$\%A_e = \frac{A_0 - A_e}{A_0} \times 100 \qquad (1)$$

$Q_e$, amount adsorbed per unit weight of adsorbent at equilibrium (mg $g^{-1}$) was calculated using the following equation. Where $M_o$ and $M_e$ are the initial and final concentrations of copper (II) ions in solution (mg $L^{-1}$), respectively [4-20].

$$Q_e = \frac{(M_0 - M_e)V}{W} \qquad (2)$$

where W is the mass of gamma alumina nanoparticles (g) and V is the volume of the solution (L). To evaluate the thermodynamic properties of the adsorption process, 0.3 g of gamma alumina nanoparticles was added into the 100 ml solution with pH of 3.0 and initial copper (II) ions concentration ranging from 50 mg. $L^{-1}$ in every experiment. Each solution was shaken continuously for 60 min [4-20].

## RESULTS AND DISCUSSTON

### *The Effect of pH*

The effect of pH on the metal adsorption by the Bentonite was studied in the pH region between 2 and the pH of solution (5 and 6), where the material exhibits chemical stability. The pH was limited to values less or equal to 6 because of precipitation at higher pH. Solution pH is one of the most important parameters to determine [11-22]. Batch studies at different pH (2-8) were conducted by soaking the adsorbent in 0.04 g.L$^{-1}$ of copper (II) ions in each microcosm. Each container was agitated (156 rpm) for 1 h at 20$^{o}$C. Table 1 illustrate the effect of the pH of the solution on the adsorption percentage of copper (II) ions, adsorbed onto gamma alumina nanoparticles. The best results were obtained at pH=6 for copper (II) ions. The decrease of the adsorption capacity in alkaline pH may be attributed to the precipitation Cu $(OH)_2$.

**Table 1**. The effect of initial pH of the solution on the adsorption percentage (%A) of copper (II) ions ($M_o$ = 0.04 g.L$^{-1}$, W gamma alumina nanoparticles = 0.03 g, T = 293 K, $t_c$ = 60 min)

| pH | %Ae |
|---|---|
| 2 | 34.81 |
| 3 | 64.54 |
| 4 | 68.75 |
| 5 | 73.52 |
| 6 | 73.56 |
| 7 | 73.55 |
| 8 | 73.52 |

### *The Effect of Adsorbent Dosage*

Microcosms with different adsorbent doses (0.01-0.07 g) were amended with 0.04 g.L$^{-1}$ of copper (II) ions in aqueous solutions. The rate of adsorption was monitored at the following optimum conditions: pH of 6, for 60 min at 20$^{o}$C. The effect of gamma alumina nanoparticles dosage on the adsorption percentage of copper (II) ions is shown in table 2. The best results were obtained at W gamma alumina nanoparticles =0.04 g for copper (II) ions.

**Table 2**. The effect of gamma alumina nanoparticles dosage on the adsorption percentage (%A) of copper (II) ions (Mo= 0.04 g.L$^{-1}$, pH=6, T=293 K, tc= 60 min)

| **W** gamma alumina nanoparticles **/g** | **%Ae** |
|---|---|
| 0.01 | 51.32 |
| 0.02 | 68.57 |
| 0.03 | 73.15 |
| 0.04 | 81.91 |
| 0.05 | 81.05 |
| 0.06 | 79.87 |
| 0.07 | 79.87 |

### *The Effect of Temperature*

The same preparation was made, except for the varying temperature conditions. The microcosm which was maintained at pH=3 was incubated at different temperatures (20-50 $^{o}$C) for a period of 60 min. Table 3 show that the adsorption percentage decreases with increasing temperature. Therefore, it may be concluded that the interaction between copper (II) ions and gamma alumina nanoparticles is exothermic in nature. Adsorption decrease may be due to the increase of the electrostatic repulsion between the copper (II) ions [4-25].

**Table 3**. The effect of temperature on the adsorption percentage (%A) of copper (II) ions ($M_o$=0.04 g.L$^{-1}$, W gamma alumina nanoparticles =0.04 g, pH=6, $t_c$=60 min)

| T/K | %Ae |
|---|---|
| 293 | 43.21 |
| 298 | 58.43 |
| 303 | 63.98 |
| 308 | 79.64 |
| 313 | 91.32 |
| 318 | 92.51 |
| 323 | 92.51 |

### *The Effect of Contact Time*

The effect of contact time, tc, on the adsorption percentage of copper (II) ions onto gamma alumina nanoparticles is shown in table 4. A rather fast uptake occured during the first 25 min of the adsorption. It became slower as the adsorbed amount of copper (II) ions reached its equilibrium value. It can be seen that the adsorption process is rapid due to the availability of very active sites on the adsorbent surface at initial stage. This may be due to the special one atom layering the structure of copper (II) ions [5-19]. At first, adsorption capacity was a slow process then, increased rapidly, it attained equilibrium and saturation gave constant adsorption value. The optimum contact time was obtained at 25 min.

**Table. 4**. The effect of contact time, $t_c$, on the adsorption percentage (%A) of copper (II) ions
($M_o$=0.04 g.$L^{-1}$, W gamma alumina nanoparticles =0.04 g, pH=6, T=318 K)

| tc/min | %At |
|---|---|
| 5 | 45.73 |
| 10 | 52.60 |
| 15 | 63.96 |
| 20 | 75.21 |
| 25 | 86.57 |
| 30. | 86.57 |

### *Adsorption Isotherm*

The experimental data were analyzed in the light of Langmuir and Freundlich adsorption isotherms .An adsorption isotherm is characterized by certain constant values, which express the surface properties of the adsorbent and so on the percentages adsorption of copper (II) ions onto gamma alumina nanoparticles as a function of initial concentration of copper (II) ions, shown in table 5.

Adsorption isotherms represent the relationship of the amount of dyes adsorbed with the adsorbent dose. These provide information about the mechanism of adsorption and the adsorptivity of the composite towards the dyes of interest. In this study, Langmuir and Freundlich isotherms were investigated. The Freundlich isotherm is an empirical equation used to model multilayer adsorption on heterogenous adsorbents, with the assumption that sites of adsorption exponentially increase with an increase in the heat of absorption. The linear form of Freundlich isotherm is given by the equation [8-20]:

$$lnQ_e = lnP + \frac{1}{n}\ln M_e \quad (3)$$

where P (L/g) and n are the Empirical Freundlich constant or capacity factor and adsorption intensity. The values of P and n are determined from the intercept and slope of a plot of Ln $Q_e$ versus Ln Me (table 5 and fig. 1) that were used to calculate the values of P and n (table 6)).

Monolayer adsorption onto the surface of the adsorbent is assumed by the Langmuir isotherm. In this model, it is

**Table 5**. Adsorption data for copper (II) ions adsorption onto gamma alumina nanoparticles (pH=6, $t_c$=25 min, T=318 K, W gamma alumina nanoparticles =0.04 g)

| Parameter | Value | | | |
|---|---|---|---|---|
| $M_0$ /g $L^{-1}$ | 0.030 | 0.040 | 0.050 | 0.060 |
| %A | 63.333 | 65.000 | 68.000 | 70.000 |
| Me / g $L^{-1}$ | 0.011 | 0.014 | 0.016 | 0.016 |
| $Q_e$ / g $g^{-1}$ | 0.024 | 0.033 | 0.043 | 0.053 |
| lnMe | -4.510 | -4.269 | -4.135 | -4.017 |
| lnQe | --3.730 | -3.411 | -3.147 | -2.938 |
| 1/Me /L $g^{-1}$ | 90.910 | 71.429 | 62.500 | 55.556 |
| 1/$Q_e$ /g $g^{-1}$ | 41.667 | 29.867 | 23.256 | 18.868 |

assumed that binding of dyes onto the adsorbent is homogeneous, and that adsorption will no longer take place once equilibrium has been established. Also, this model predicts an equal distribution of dyes between the liquid and solid phases.The linear form of the Langmuir isotherm is described by the following equation [11-23]:

$$\frac{1}{Q_e} = \frac{1}{bQ_m}\left(\frac{1}{C_e}\right) + \frac{1}{Q_m} \qquad (4)$$

where $Q_m$ (mg $g^{-1}$) is the maximum dyes to adsorb onto 1 g adsorbent and b (L/mg) is the Langmuir constant related to adsorption capacity and energy of adsorption. The slope and intercept of plot of $1/Q_e$ versus $1/M_e$ are shown in fig. 2 that were used to calculate the values of b and $Q_m$ (table 6).

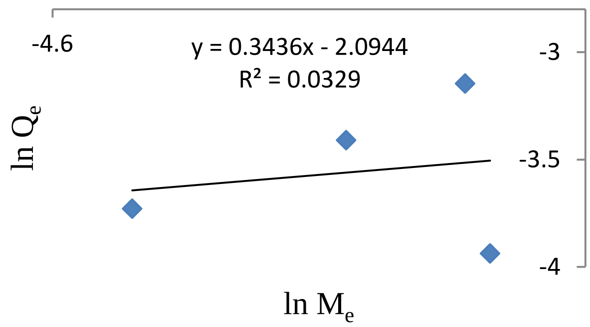


**Fig. 1**. Freundlich isotherm for copper (II) ions adsorption onto gamma alumina nanoparticles.

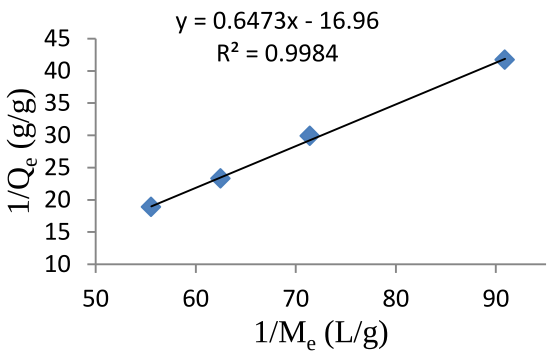


**Fig. 2**. Plot of ($1/Q_e$) versus ($1/M_e$) for copper (II) ions adsorption onto gamma alumina nanoparticles.

**Table 6.** The resultant values for the studied isotherms in connection to copper (II) ions adsorption onto gamma alumina nanoparticles at 328 K

| Isotherm | Parameter | Value |
|---|---|---|
| Freundlich | P /(L $g^{-1}$) | 0.1230 |
| | n | 2.7520 |
| | $R^2$ | 0.0329 |
| Langmuire | b / (L $g^{-1}$) | 26.2010 |
| | $Q_m$ /(g $g^{-1}$) | 0.0590 |
| | $R^2$ | 0.9984 |

**Thermodynamic Parameters**

The amounts of adsorption of heavy meal by natural bentonite are measured in temperature 288-313 K. Analysis of thermodynamics of equilibrium adsorption data can give more important information on adsorption process. Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined using the following equations. In the present study, thermodynamic parameters $\Delta H^0$, $\Delta S^0$ and $\Delta G^0$ were calculated by using the equation. The thermodynamic parameters of adsorption process can be determined from the variation of thermodynamic equilibrium constant, $K_o$ [10-28], where $K_o$ is defined as follows:

$$K_0 = \frac{a_S}{a_e} = \frac{Q_e}{M_e} = \frac{M_0 - M_e}{M_e} \qquad (5)$$

where $a_S$ and $a_e$ are the activity of adsorbed copper (II) ions and the activity of copper (II) ions in solution at equilibrium, respectively. The adsorption standard free energy change ($\Delta G^0$) is calculated according to:

$$\Delta G^0 = -RTlnK_0 \qquad (6)$$

The average standard enthalpy change ($\Delta H^o$) and the average standard entropy change ($\Delta S^o$) are obtained from the plot of equation (7):

$$lnK_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (7)$$

The ΔH° and ΔS° values obtained from the slope and intercept of van't Hoff plots are presented in table 7and fig. 3.

**Table 7**. The effect of temperature on $K_o$ values
($M_o$=0.04 g.L$^{-1}$, pH=6, W gamma alumina nanoparticles =0.04 g, $t_c$=25 min)

| T/K | lnK |
|---|---|
| 298 | 0.340 |
| 303 | 0.574 |
| 308 | 1.364 |
| 313 | 2.353 |
| 318 | 2.514 |

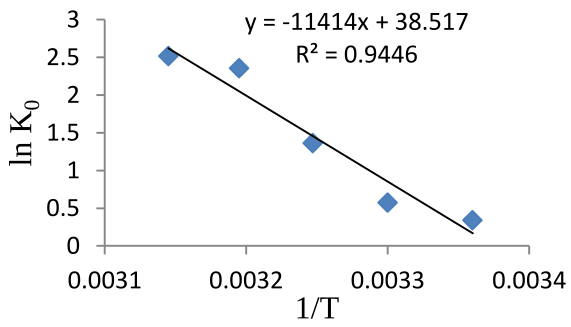


**Fig. 3**. The effect of temperature on equilibrium constant values.

**Table 8**. Thermodynamic parameters for adsorption copper (II) ions onto gamma alumina nanoparticles

| T /K | ΔG°/J.mol$^{-1}$ | ΔH°/J.mol$^{-1}$ | ΔS° /J.mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| 298 | -843.491 | | |
| 303 | -1423.356 | | |
| 308 | -3492.667 | 94895.996 | 320.230 |
| 313 | -6124.076 | | |
| 318 | -6645.978 | | |

The obtained values of thermodynamic parameters ($\Delta G^0$, $\Delta H^0$, $\Delta S^0$) are listed in table 8. The positive value of $\Delta H^0$ suggests that the interaction of adsorbed copper (II) ions with gamma alumina nanoparticles is an endothermic process, which is supported by the decreasing of the amount of copper (II) ions adsorption with increasing temperature. The positive value of $\Delta S^o$ showed an increased randomness during copper (II) ions adsorption. The negative values of $\Delta G^0$ reveal the fact that the adsorption process is spontaneous and the positive values of $\Delta H^0$ reveal the fact that the adsorption process is endothermic.

## CONCLUSION

Taking into account the results, we have considered it of great interest to assess the ability of locally available bentonite for the adsorption of copper (II) ions from aqueous solutions in the batch technique and optimization of conditions for its adsorption. The results of this work show that gamma alumina nanoparticles is an effective adsorbent for the removal of copper (II) ions from aqueous solutions. The experimental data correlated reasonably well by the Langmuir and Freundlich adsorption isotherms and the isotherm parameters were calculated. Results showed that the maximum adsorption capacity of the adsorbent occurred in pH of 6.0 and the Langmuir isotherm model was fitted well with adsorption data, thus, indicating the applicability of monolayer coverage of copper (II) ions on gamma alumina nanoparticles surface. The temperature variations have been used to evaluate the values of $\Delta H^0$, $\Delta S^0$ and $\Delta G^0$. Thermodynamic analysis revealed that the adsorption process is endothermic (The positive value of $\Delta H^0$) and spontaneous in nature (The negativ value of $\Delta G^0$).

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**مجله شیمی فیزیک و شیمی نظری**
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# حذف یون‌های مس (II) از محلول آبی با استفاده از نانوذرات گاما آلومینا

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## چکیده

جذب سطحی یکی از کارآمدترین روش‌های حذف فلزات سنگین به عنوان یکی از مهم‌ترین آلاینده‌های منابع آبی به شمار می‌آید. بنابراین، هدف این مقاله یررسی حذف یون‌های مس (II) از محلول آبی با استفاده از نانوذرات گاما آلومینا به عنوان جاذب بود. از روش ناپیوسته برای مطالعه پارامترهای مختلف شامل زمان تماس، دما، غلظت اولیه مس pH و مقدار نانوذرات گاما آلومینا استفاده شده است. غلظت یون‌های مس (II) با استفاده از طیف‌سنج UV-vis در طول موج ۳۹۰ نانومتر اندازه‌گیری شد. از ایزوترم فرندلیچ و لانگمویر برای تجزیه و تحلیل ایزوترم استفاده شد. حداکثر جذب در pH=6 برای جذب نانوذرات گاما آلومینا صورت گرفت و با کاهش pH میزان جذب کاهش می‌یابد. مشخص شد که ایزوترم لانگمویر با داده‌های ما مطابقت بیشتری دارد. طبق تجزیه و تحلیل ترمودینامیکی، فرایند جذب خودبه‌خود و گرماگیر است.

**کلید واژه‌ها:** یون‌های مس (II)، جذب سطحی، ترمودینامیک، نانوذرات گاما آلومینا

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