Effect of Cu^{2+} Concentration on Adsorption - Sorption Mechanisms, Modes, Critical Concentration Edge, and Spontaneity of Octahedral [Cu (H$_2$O) $_6$]$^{2+}$ on γ Alumina

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

ABSTRACT

Aims: To apply a fast, & save method for water treatments by using physical removal of toxic metal ions such as Cu^{2+} by adsorption at solid insoluble, non toxic, reusable adsorbent as γ Alumina. to indicate the effects of Cu^{2+} concentrations ranges on the adsorption modes, mechanisms, maximum efficiency, and the thermodynamic parameters indicating spontaneity of the processes. As we have to get strong adsorption to avoid desorption of ions to solution but the low apparent adsorption spontaneity was contradicted (not inconsistent) with the produced high strength of adsorption) encourage us to determined the true free energy change for each adsorption mode by studying the adsorption mechanism and energy relations of each adsorption mode.
Place and Duration of Study: Benghazi University, Chemistry Department, Benghazi, Libya between Sep 2009 and Dec 2011.
Methodology: Solutions of concentrations from, 1.5 to 15.5 x10^{-3}M of Cu^{2+} which resembling that of industrial, agriculture, and waste water. Cu^{2+} form cupric water octahedral complex ion, (CWOCl) [Cu(H$_2$O)$_6$]$^{2+}$ was prepared by dissolving in buffer solution to be maintained at pH = 4.5. The batch technique of adsorption test was followed in testing 50 ml of each test solution which was simultaneously shacked with 0.5 gram adsorbent (γ Al$_2$O$_3$) for 60 minutes with shacking rate of 300 cycle per minute using water

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thermostat shaker at 30ºC. The amount of Cu^{2+} adsorbed was determined by measuring the difference of its concentration before, and after adsorption by measuring the optical density of the blue $[Cu (NH_3)_4)]^{2+}$ at pH=11 formed by adding NH_4OH to Cu^{2+} solution, using spectroscopic method with a beam of wave length 580nm.

Results: The results were applicable to Langmuir, and Ismaeel adsorption isotherms all over this concentration range but it show a deflection of Langmuir line, and deflection with splitting of Ismaeel line at the same equilibrium concentration edge (CE)= 3.3 x 10^{-3}mole which divided the isotherms into two low, and higher concentrations ranges. The same divisions were occurred also to the lines of the relations of the solution concentration versus adsorption rate, the surface coverage fraction θ, the adsorption efficiency % and spontaneity indicating two modes and mechanisms of adsorption before and after CE.

Conclusion: We have to avoid applying adsorption processes on concentrations higher than the CE, by using dilution with pure water to just lower the concentration than CE or by increasing the mass of adsorbent. To gain maximum (adsorption- sorption), Spontaneity, Efficiency, Rate and Surface coverage %.

Applying Ismaeel adsorption isotherm, enable to know the adsorption modes and activation energy used to release and replace the water molecules already adsorbed on adsorbent surface, and determining the true value of adsorption free energy change which identify the adsorption type as, chemisorptions confirmed by the high adsorption spontaneity as ΔG true reached more negative than -296 KJM^{-1}. The length of the long axes of (CWOCl) was exactly calculated from experimental results, which was difficult to be determined by (XAFS) technique.

1. INTRODUCTION

This work aimed to apply a fast & save method for water treatments by using physical removal of toxic metal ions such as Cu^{2+} by adsorption at solid insoluble, non toxic, reusable adsorbent as γ Alumina. to indicate the effects of Cu^{2+} concentrations ranges on the adsorption modes, mechanisms, maximum efficiency and the thermodynamic parameters indicating spontaneity of the processes. As we have to get strong adsorption to avoid desorption of ions to solution but the low apparent adsorption spontaneity indicated by the values of apparent free energy change which was contradicted (not inconsistent) with the produced high strength of adsorption) which encourage us to determined the true free energy change for each adsorption mode by studying the adsorption mechanism and energy relations of each adsorption mode.

It was reported that Copper contamination of environment arises from industrial and agricultural emissions, it is also found as wastes and byproduct from the metal mining processing industry, and from agricultural sources such as fertilizers, fungicidal sprays, and animals waste [1-4]. Researches indicated that copper at sufficiently high concentrations, and when it is in a mobile form become toxic and suggested that copper toxicity in aqueous system may be a function of the free ion concentration rather than of total copper concentration [5]. Studies concerned the transport of Cu^{2+} in soils and aquatic systems where it is adsorbed on soil surfaces as an important process regulating metal ion concentrations in nature [6]. The USA Environmental Protection Agency (EPA) Reports set the Drinking Water Standard Action Level for Treatment Technique = 1.3 parts per million (P.P.M.). Some people who drink water containing copper in excess of the action level may,

with short term exposure, experience gastrointestinal distress and with long-term exposure may experience liver or kidney damage. People with Wilson's disease, should consult their personal doctor if the amount of copper in their water exceeds the action level [7].

Many of the researches in the field of water treatments for removal of heavy metals specially the copper of high toxicity and lower action level for treatments. One of the best green physical removal methods were the adsorption of its ions on non toxic insoluble adsorbent such as γ Alumina [8]. Some of a numerous studies have been conducted measuring the adsorption of metal ions onto oxide surfaces. Sorption is strongly pH dependent, as it is increasing with an increase in pH. Considered that there is a narrow pH range (the adsorption pH edge) where adsorption increases from zero to 100% [4,9].

The nature of Cu^{2+} adsorption at non crystalline alumina was studied over a range of equilibrium pH (4.5–7.5) and Cu^{2+} concentration (10^{-3}–10^{-8} M) by electron spin resonance (ESR). Available chemisorptions sites at pH 4.5 were the most numerous for non crystalline alumina (1m mole/100g), as indicated by the relative strength of the rigid-limit ESR signal attributed to Cu^{2+} desorbed at discrete sites. The chemisorptions process involved immobilization of Cu^{2+} by displacement of one or more H_2O Legends by hydroxyl or surface oxygen ions, with the formation of at least one Cu-O--Al bond. As the pH was raised from 4.5 to 6.0, essentially all of the solution Cu^{2+} appeared to be absorbed by the solids. However, the non crystalline alumina chemisorbed much of the total adsorbed Cu^{2+} (10m mole/100 g. adsorbent) [10].

The adsorption of Cu^{2+}, on non crystallin Alumina, coverage of approximately μmol/m^2, the collected X-ray absorption fine structure (XAFS) data for several Cu^{2+} containing model compounds. For comparison with the sorption sample data. Detailed analysis of these model compounds indicates that the bonding of second neighbors surrounding a central Cu absorber determines whether these second neighbors can be detected by XAFS. The XAFS results of Cu^{2+} sorption samples are consistent with the presence of Jahn -Teller distorted $[Cu^{2+}(O,OH)_6]$ octahedral, with four equatorial Cu-O bonds (1.95 Å) and two longer axial bonds; the axial Cu-O bonds are difficult to characterize quantitatively by XAFS spectroscopy. Cu^{2+} sorbed on γ-Al_2O_3 is present as a mixture of monomeric, dimeric and perhaps a small number of oligomeric hydroxo-bridged $Cu(O,OH)_6$ species with a Cu-Cu distance of approximately 2.95 Å [11].

Due to the importance of clay minerals in metal sorption, the studies have attempted to derive mechanistic models that describe adsorption processes. This study conducted X-ray absorption fine structure spectroscopy (XAFS) and electron paramagnetic resonance (EPR) spectroscopic experiments on the cupric ions sorbet on smectite clays using suspension pH and ionic strength as variables. At low ionic strength, results suggest that Cu is sorbet in the inter-layers and maintains its hydration sphere. At high ionic strength, Cu atoms are excluded from the interlayer and sorbet primarily on the aluminol functional groups Interpretation of the XAFS and EPR spectroscopy results provides evidence that multinuclear complexes are forming. Fitting of extended X-ray absorption fine structure spectra revealed that the Cu-Cu atoms in the multinuclear complexes are 2.65) Å apart and have coordination numbers near one [8,12]. Research was aimed at soluble copper (Cu^{2+}) removal from aqueous solution (polluted water, such as industrial, and agriculture west water [4]. This metal was chosen because of its high toxicity, and because it is considered as the most common pollutants present in liquid industrial waste. Under optimized adsorption conditions show that 97,84% of copper, can be removed from the liquid waste [4,13]. The Adsorption isotherms represent the relation between the adsorbent concentration and the amount

adsorbed at certain constant temperature, and conditions as, freundlich, Helsly, Langmuir, and Ismaeel adsorption isotherms [4,13-17]. The obtained results in the present work were applicable to Ismaeel and Langmuir adsorption isotherms overall the test concentration rang. (1.5 – 15 X10^{-3} M.)[18,19].

2. METHODOLOGY

2.1 Materials

All chemicals used were of analytical grad, the water used in preparation of test solutions and final glass wears washing was of 2nd distilled water of conductivity (4µs), the adsorbent was γ-Al_2O_3 and Cu SO_4. $5H_2O$ was used as a source of Cu^{2+} ions. Ammonium hydroxide for adjusting pH of octahedral Cu^{2+} complex ions solutions as Per [10]. A set of 50 ml of test solution as 5 samples of each concentration (for reliability and repeatability of the results) was marked to be ready to simultaneously test at the same condition using the batch technique.

2.2 The Solutions

Cu SO_4, $5H_2O$ was used as a source of Cu^{2+} ion. A stock of buffer solution of pH = 4.5 was prepared as a solvent for preparation of Cu^{2+} solutions of concentrations100, 150, 200, 250, 500, 625, 700 and 1000 (P.P.M.) of Cu^{2+}) [100ppm = 1.57366 x 10^{-3} M]. The pH of $[Cu(H_2O)_6]^{2+}$ test solutions was maintained at 4.5 to favor identical strong chemisorptions condition for all concentrations.

2.3 Equipments

Glass wears of different types and volumes were used in solution preparations, measuring, keeping and for test solution during adsorption test processes.

Auto calibrated digital pH meters for adjusting and controlling the pH value of test solutions before and during test time.

Water thermostat shaker of capacity of 24 samples, with variable shacking rate, time and temperature

Digital spectrometer to enable the measuring of absorption of wave of length 580 nm to give maximum absorption by test solution.

2.4 The Adsorption Test Technique

The batch technique of adsorption test [15,18,4] was followed, in testing 50 ml of each test solution. Simultaneously shacked with 0.5 gram adsorbent (γ Al_2O_3) for 60 minutes with shacking rate of 300 cycle per minute using water thermostat shaker at 30 ± .01ºC.

The test solutions was filtrated, pipette 25ml of each filtrate in 50ml measuring flasks, complete till mark with 1:1 ammonium hydroxide solution of pH = 11.5 to form deep blue color solution of $[Cu(NH_3)_4]^{2+}$ at pH = 11 for spectroscopic measurements of Cu^{2+} concentrations, using absorption of light beam has wave length 580nm, for constructing calibration curve used in determining the initial concentration (Ci.), and final concentration

(Cf.) for each test solution maintained at 4.5 to favor identical strong chemisorptions condition for all octahedral Cu^{2+} complex ions.

3. RESULTS AND DISCUTION

3.1 Adsorption Isotherms

The experimental results are applicable to Langmuir, and Ismaeel adsorption isotherm [18,19], the adsorption isotherms equations and its calculations are illustrated as follows:

The amount of Cu^{2+} adsorbed = ΔC M. = (C i.– Cf.) M.

The number of moles adsorbed per gram of alumina N= (ΔC M. x volume L.) / g. adsorbent = (ΔC Mx 50ml /[1000ml x 0.5 g] = mole /g. adsorbent. Langmuir adsorption isotherm is represented by a straight line equation as

$$Cf / N = (Cf. / Nm) + 1/ (K \times Nm) \qquad (1)$$

where Ci. and Cf. are the initial and final concentrations, respectively, (Nm) is the number of moles needed to form mono layer adsorbate, K is the adsorption equilibrium constant. The value of (Cf./N) was plotted versus Cf. to give straight line Fig.1 denoted by O, of slope = (1/Nm) and intercept = (1/K. Nm) from which the value of Nm and K was determined. The (apparent net) adsorption free energy change, ΔG app. = - 2.303 RT log K, and The surface coverage fraction θ = (N/Nm). The calculated values of log K, Nm and ΔG app. Before and after CE are given in Table 1.
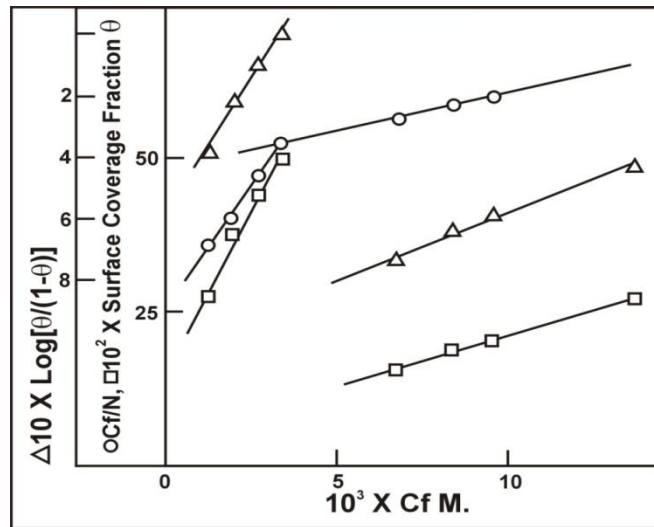

Fig. 1. Reveal the relation between Cf. M. versus; Cf/N (Langmuir Adsorption isotherm) marked by O, log [θ / (1- θ)] Ismaeel adsorption Isotherm marked by $\triangle$ and the surface coverage fraction (θ) marked by $\square$, for the sorption / adsorption of [Cu (H$_2$O)$_6$]$^{2+}$] [to γ-Al$_2$O$_3$ at 30ºC

Table 1. Give a comparison of the results deduced from Langmuir adsorption isotherm before and after Cu^{2+} concentration edge CE for the sorption/adsorption of [Cu (H$_2$O)$_6$]$^{2+}$ to γ-Al$_2$O$_3$ at 30ºC with short comments

The results	The first low conc. range before conc. edge	The second high conc. rang, after conc. edge	↓↑after conc. edge
1. Slope of Langmuir ads. line denoted by ○Fig. 1 =	7946	1308	Decreases↓
2. Nm = moles	1.258 x 10^{-4}	7.647 X10-4	Increases↑
3. Log K =	2.4938	1.4353	Decreases↓
4. ΔG app. = - 2.303 RT log K=	- 14.475 kJ.M-1	-8.331 kJM-1	Spontaneity decreases↓
5. Decrease of efficiency % per 1M increase of Ci , Fig. 2	4417	193.548	Decreases↓
6. Adsorption rate constant Kr =	3.25 x 10^{-1} S^{-1} [1st order reaction]	3.15 x 10^{-1} S^{-1} [1st order reaction]	Slight decrease

Ismaeel adsorption isotherm concerning two adsorbate, one have a duel enhancing and competing action denoted by (2) and the second is the main adsorbate [Cu(H$_2$O)$_6$]$^{2+}$ cupric water octahedral ion (CWOI) denoted by (1). The isotherm also concerning the size ratio of the octahedral ion to that of competing water molecule (r$_{12}$) and the heterogeneity parameter of adsorbent surface (m). Ismaeel adsorption isotherm equation (2) is,

$$\log [\theta /(1- \theta)] = \log [r_{12} / m\ C_2] + C_1 .r_{12}.C_2 . m .\log K \tag{2}$$

Plotting log [θ /(1- θ)], verses C$_1$ gave straight line denoted byΔ in Fig.1, with:

Slope = r$_{12}$ C$_2$ .m. log K   …………………………….……………… ……. (2a)

and intercept with Y axis= log [r$_{12}$ / C$_2$ m]. …………………….…….……………… (2b)

Where C$_2$ is the molar concentration of the competing water molecule for adsorption already adsorbed on the adsorbent surface, and (C$_1$) is the concentration of the main adsorbate (CWOI).By substitute the value of Log K from Langmuir (Table 1.) in equation (2a) and solving with equation (2b), the values of the size ratio (r$_{12}$) and the surface heterogeneity parameter (m), were determined and its values were given in Table 1.

The experimental results were applicable to the three relations as it gave straight lines but it was noticed that each line is divided into two parts one in the lower concentration range up till Cf =3.3m. M. represents a concentration edge CE after which the Langmuir line deflected to lower positive slope at higher concentration rang till Cf = 13.**7** x10^{-3} M. The line represents Ismaeel adsorption isotherm suffering the same deflection with splitting into two parts at the same CE. The line represents the relation of (θ), versus the equilibrium concentration Cf (Fig. 1), (denoted by □**)** shows an increases of (θ), with slope =106.**25**, till it reach (0.50) at the CE then it was sharply failed to (θ) = 0.10, to start the increase again but with lower slope to reach 0.25 at Cf =13.7x10^{-3}.M.

3.2 The Adsorption Rate and Efficiency

Fig. 2. reveal the relation of adsorption rate (M./S) marked by triangles Δ, versus Ci. which represented by straight lines with slope = the rate constant (Kr). The figure showed the same previous behavior of CE, after which the second part started with different slope values. The decreases of adsorption efficiency % versus the increase of the initial concentration Ci. marked by circles O is greater in the first region than that of the second region. All these results indicated in Fig. (1 and 2) presents a question to be answered. According to [8], that at certain concentration the adsorption is a pH dependent, and there was pH edge at which the adsorption changed sharply and since our pH is maintained constant at 4.5, we considered the concentration which divide the concentration range into two region as the CE [concentration edge]**.**
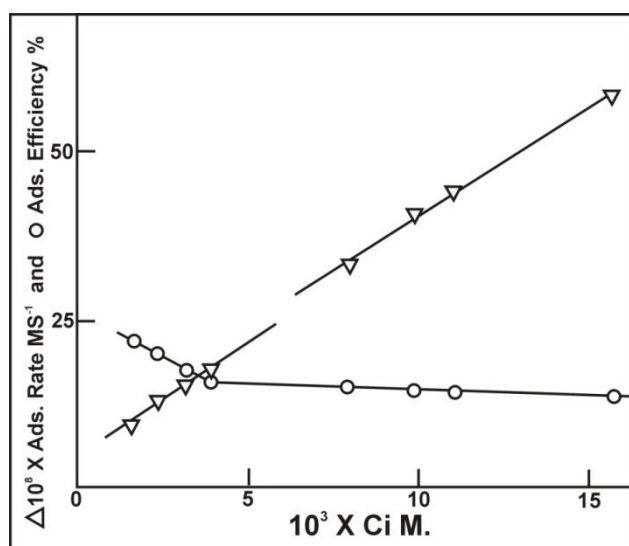

**Fig. 2. Reveal the change of the adsorption rate (MS^{-1}) marked by Δ
and adsorption efficiency % marked by O , versus the change of Ci M
for the sorption / adsorption of [Cu (H$_2$O)$_6$]$^{2+}$ to γ-Al$_2$O$_3$ at 30ºC**

3.3 Adsorption Modes

In the light of *the* results deduced from all these relations, and the results given by [10,11,20] of (X-ray Absorption Fine Structure) (XAFS) Spectroscopy of Cu^{2+} sorption, samples which were consistent with the presence of Jahn -Teller distorted [Cu (H$_2$O)$_6$]$^{2+}$ octahedral, with four equatorial Cu-O bonds (1.95 Å) and two longer axial bonds. In our work, we postulate the existence of horizontal and vertical adsorption modes before and after CE respectively as illustrated by the schematic diagram in Fig. 3. After CE, Langmuir adsorption isotherm show lower, slope, spontaneity represented by the values of ΔG, leads us to postulate the existent of two different adsorption modes before and after the edge this postulate is confirmed by the increases of (Nm) after the edge which means that the adsorption mode after the edge let the octahedral [Cu (H$_2$O)$_6$]$^{2+}$ ion cover less surface aria than that covered before the edge (at low concentration range). Accordingly we postulate that the complex ion strongly sorbet horizontally into the γAl$_2$O$_3$ with higher rate constant   3x10^{-5} S^{-1}. The strong horizontal sorption occurred through tow short Cu—O bonds (1.95 Å) of the octahedral ion to

form two short strong bond Cu-O-Al. So Cu had strengthen sorption in the inter layers was confirmed by [9,11,20,21] rationalized that at high ionic strength, after CE, Cu ions are excluded from the interlayer and sorbet primarily on oxygen of γ-Al$_2$O$_3$ [8,12] this exclusion explain why the surface coverage fraction (θ) reach 0.50 at the concentration edge and fail to 0.10 after the edge and start to increases with low rate, where low spontaneity which confirmed our postulate that the octahedral ion is weakly adsorbed vertically on the oxide surface through only one of the octahedral longer Cu—O bond to form the vertical longer Cu-O-Al bond of length (L) [11], where the CWOCI of this mode cover lower surface aria than that of the horizontal one as shown in Fig. 3. Where it equal the aria of the square of the CWOCI.
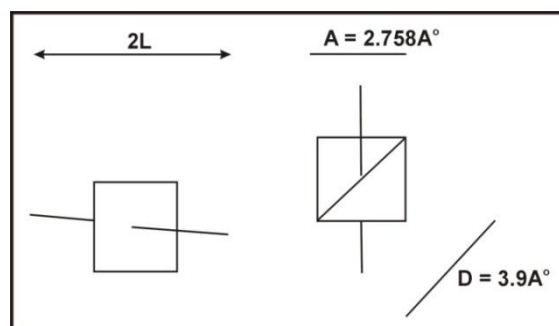

Fig. 3. Schematic diagram represents the postulated horizontal and vertical modes of sorption, of [Cu (H$_2$O) $_6$]$^{2+}$ CWOCI on γ Alumina at 30ºC at the left and right hand side respectively

3.4 Calculations

3.4.1 From Table 1

The results of Ismaeel isotherm show the size ratio (r$_{12}$) of the adsorbed complex ion to that of adsorption competing water molecules as; (r$_{12}$) of the horizontal adsorption = 4.41 and (r$_{12}$) of vertical adsorption =1.727. So the aria covered by horizontal mode / that covered by vertical mode = 4.41 / 1.727 = 2.5536.

From the dimensions indicated in Fig. 3. since the aria covered by vertical adsorption equals the aria of the square of the Octahedral ion = (square side A)^2 = (2.7577)^2 = 7.605 Å^2

The aria covered by horizontal mode = 7.6o5 x 2.5536 =19.42013 Å^2 from which the longer Cu-O-Al bond length which, was difficult to characterize quantitatively by [10]. by using XAFS (X-ray Absorption Fine Structure Spectroscopy), can be calculated as follow; 19.42013 Å^2 = 2L X (side of the square A) =2L x (2.7577 Å) = 5.5154 L. The longer Cu-O-Al bond length, L = 19.42013 / 5.5154Å =3.521 Å
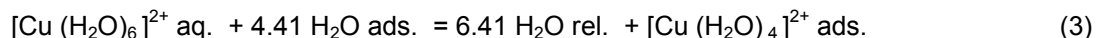
3.4.2 The adsorption specific aria

The adsorption specific aria of CWOCI on γ Alumina before CE was calculated from the relation adsorption specific aria = Nm x aria covered by molecule x NA Adsorption = 1.25 x 10^{-4} x 19.42013 Å^2 x10^{-20} x 6.022 x 10^{23} = 14.6185 m^2 /(g γ Alumina). After CE,

the adsorption specific aria $= 7.647 \times 10^{-4} \times 7.605\text{Å}^2 \times 10^{-20} \times 6.022 \times 10^{-23} = 35.0212$ m^2/ (g. γ Alumina).

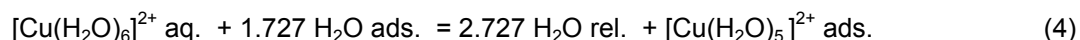### 3.4.3 Adsorption mechanism and energy relations

For each adsorption mode were studied as illustrated by Equation (3) which represents the adsorption mechanism Before CE, where one mole of CWOCI replace 4.41 moles of the already *adsorbed* water molecules (r_{12}) and released two of the short 4 equidistant water legends to be adsorbed on γ Al$_2$O$_3$ by forming 2 bonds with 2 oxygen of the oxide.

$$[\text{Cu} (\text{H}_2\text{O})_6]^{2+} \text{ aq. } + 4.41 \text{ H}_2\text{O ads. } = 6.41 \text{ H}_2\text{O rel. } + [\text{Cu} (\text{H}_2\text{O})_4]^{2+} \text{ ads.} \qquad (3)$$

The heat of releasing one mole of water molecule either from the oxide surface or from the legends, of CWOCI was considered to equals the ΔH evaporation of water $= + 44$ kJM^{-1} as per [22]. Accordingly from equation (3) the energy needed to release 6.41mole of water $= 6.41 \times 44.01 = + 282.1041$ kJM^{-1} which consumed from the true ΔG of adsorption as follow. ΔG true + ΔH released = ΔG apparent or ΔG true = ΔG app. - ΔH released, ΔG true = -14. 475 - 282.1041= - 296.5791 kJM^{-1} indicating high chemisorptions spontaneity of the Horizontal sorption mode in the inner layer oxide pores. As the concentration increased, the remainder apparent energy released by the sorption processes was accumulated with the released water inside the pores of the oxide inter layer. At CE the situation is that the rate of adsorption is higher than that of the desorption due to the immobilized sorbet complex ion through 2 strong chemisorptions bonds, the crowded water molecules inside the pores of interlayer which cant scab to the outer surface unless it has energy to overcome the external higher pressure than that of the inside pressure, at the same time water molecules competing with the incoming CWOCI into the pores. Accordingly at any increase more than CE, the sorbet ions were desorbed and extruded on the outer surface to start adsorption processes in agreement with the experimental results indicated the change of the surface coverage (θ) verses the increase of Cf in Fig. 1. This desorption and extrusion processes consumed the accumulated energy.

From the previous, it was confirmed that the concentration edge (CE) is a function of the pores size of inter layer, the adsorbents molecular size, the sorption mode, the apparent sorption free energy ΔG app. (the net free energy change) which enhance the extrusion processes. Similarly, after the CE where CWOCI adsorbed by vertical mode according to the mechanism illustrated by equation (4) where (r_{12}) = 1.727, so one mole of complex ion replace 1.727 moles of adsorbed water molecules and released one of its axial water legends.

$$[\text{Cu}(\text{H}_2\text{O})_6]^{2+} \text{ aq. } + 1.727 \text{ H}_2\text{O ads. } = 2.727 \text{ H}_2\text{O rel. } + [\text{Cu}(\text{H}_2\text{O})_5]^{2+} \text{ ads.} \qquad (4)$$

From the results in Table 1 and from equation (4) ΔG app. = -8.331 kJM^{-1}, ΔH rel. = 2.727 $\times$ 44 = 119.988 kJM^{-1}.

The use of adsorption isotherm as Ismaeel adsorption isotherm which gave very useful data as the size ratio (r_{12}) of adsorbate molecule or ions to that of adsorption competing molecule or ion, which enable to know the adsorption mode, and activation energy used to release and replace water, the ΔG true = - 8.331 -119.988 = - 128.319 kJM^{-1} which is les negative than that of horizontal mode = - 296.5791 kJM^{-1} given by equation (3), indicating chemical adsorption less spontaneous than that before CE due to change of the covered surface and adsorption mode, to be through one vertical longer weaker bond only, which covering lower

surface aria, a comparison the results deduced from Ismaeel adsorption Isotherm before and after CE are given in Table 2.

So we have to avoid applying adsorption processes on solutions of Cu^{2+} concentrations higher than CE (practically by dilution with pure tab water to reach a concentration lower than CE or by increasing the mass of adsorbent, to gain maximum, Spontaneity, Efficiency, Rate and surface coverage.

Table 2. Give a comparison of the results deduced from Ismaeel adsorption isotherm before and after Cu^{2+} concentration edge CE for the sorption / adsorption of $[Cu(H_2O)_6]^{2+}$ to γ-Al_2O_3 at 30ºC. with short comments.

Results	The first low conc. range before conc. edge CE	The second high conc. rang, after conc. edge CE	Comments on result value ↓↑after conc. edge
Slope of Ismaeel line	164.444	44.828	Decreases↓
Intercept with Y axis	-.58	-1.02	decreases↓ (be more –ve.)
The surface heterogeneity parameter (m)	.302	.106	decreases ↓
r_{12} values	r_{12} hor. =4.41	r_{12} vert. =1.727	decreases↓
Postulated adsorption mode	Horizontal adsorption mode	Vertical adsorption mode	
r_{12} hor./r_{12}vert.= $r_1$hor. /r_1 vert.	----------------------	----------------------	$r_1$hor./ $_1$ vert. =4.41/ 1.727 = 2.554
True surface aria covered by one molecule (Fig.3)	=7.605 x 2.554 = 19.42317 $Å^2$	= $(A)^2$ =$(2.7577)^2$ =7.605 $Å^2$	decreases↓
ΔG true =ΔG app.- ΔH vab.	=-14.475 -282.04 =-296.515 KJM^{-1}	-8.331-119.989 = -128,319KJM^-	Spontaneity decreases↓
The adsorption specific aria	14.6185 m^2 / (g. Alumina)	35.0212m^2 / (g. Alumina)	increases↑

4- CONCLUSION

At constant pH value at high Cu^{2+} concentration there is concentration edge CE after which the sorption processes lose most of the gained properties at lower concentration before the edge such as sorption Spontaneity, Efficiency, Rate and surface coverage fraction, as a result of the change of adsorption mode. So we have to avoid applying adsorption processes on solutions of Cu^{2+} concentrations higher than CE (practically by dilution with pure tab water to reach a concentration lower than CE).

Since the results were applicable to both Langmuir, and Ismaeel adsorption isotherms, it enable to determine the ratio of the aria covered by the complex ion in both of horizontal and vertical mode of adsorption Table 2 by substituting the value of equilibrium constant (K) from Langmuir in Ismaeel adsorption equation to determine the ratio of the surface aria covered by one molecule (CWOCI) in horizontal to that in case of vertical mode of adsorption, [r^1 hor./r^1 vert.] which enable to determined the aria covered by the horizontal mode, from which the length of the long axe of (CWOCI) was exactly calculated from experimental

results, which was difficult to determined by (XAFS) technique. The use of [r_1 hor. / r_1 vert.] confirm the postulated adsorption modes.

Study of the adsorption mechanism and replacing the water molecules already adsorbed on adsorbent surface by the (CWOCI) and energy relations enable to determine the true value of ΔG in each adsorption mode, which identify the adsorption type.

From the relation of the adsorption rate versus concentration gave the rate constant Kr, indicting the adsorption reaction order, which was needed to calculate the adsorption activation energy.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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