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Influence of Vitamin C on Copper Electrorefining from Acidic Solution of Copper Sulfate

F.M. Abouzeid

Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

Corresponding author: Tel: +203 4943959; E-mail: fatmaabouzeid44@yahoo.com

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Electrorefining of copper in the presence of vitamin C was studied using potentiodynamic polarization method. The effect of operating conditions including sulphuric acid concentration, temperature and vitamin C concentration on limiting current. The results show that Cu deposit from its acidic solution of copper sulfate and rate of deposition decrease with increasing the concentration of suphuric acid. Vitamin C is a suppresser with the strongest action on copper electrodeposition and inhibition efficiencyincreased by increasing vitamin C concentration. The activated parameters were estimated and discussed. The adsorption of vitamin C on cathode copper surface in the acid solution was found to obey Kinetic-thermodynamic adsorption isotherm. The influence of vitamin C on morphology of electrodeposited powder was studied. Addition of vitamin C to copper bath exhibits a strong influence on the microstructure (refining the deposit).

Keywords: Copper refining, Vitamin C, Scanning electron microscope, Current efficiency.

INTRODUCTION

Within the numerous operations and processes of the metallurgical industry, one which has become widely known for its varied applications is metal electrodeposition. This process is used with very diverse aims, for example: protection against the many forms of corrosion, including its synergistic associations with mechanical phenomena, metal processing (electrowinning and electrorefining). Copper electrodeposition from acid solution, in the presence of superficial active substances, such as organic nitrogen compounds and inorganic ions, like chloride ions, was extensively studied in the literature in the past decades[1-5].

In most of these studies, it is revealed that such compounds act as inhibitors for the copper electrodeposition process through their adsorption at the metal-electrolyte interface. The presence of the organic additives in the electrolyte solution produces a decrease of the cathodic peak current directly proportional to the concentration of the additives. The overall effect of the organic additives is to inhibit the nucleation process and to shift the reduction peak potential to more negative values[6].

Nevertheless, the superficial active molecules are not permanently adsorbed on the same cathodic areas; at some point description and re-adsorption occur in some other cathodic areas where the interface concentration of the cations is reduced[7]. Therefore, new crystallization germs can make easily on the free cathodic areas. Many of these substances, depending on the electrolyte acidity or basicity, are able to form oligomers by polymerization, at electrode potentials closed to the copper reduction potential. Therefore, the selection of appropriate additives is very important.

The rate determining step at current densities closed to the limiting current density is the mass transport[8,9] but the copper crystal growth, with a layered structure takes place at lower current densities where the charge transfer across the electric double layer is the rate determining step[10].

Although the organic additives generally adsorb on the copper electrode surface, they may exhibit dissimilar catalytic effects. For example, it has been found that benzylamine has a pronounced catalytic effect on the hydrogen evolution reaction in acid solution[11] but the same compound inhibits the Cu^{2+} reduction process[12,13]. The protonation of the benzylamine molecule in acid solution modifies its electronic structure and thus the dipole moment vector, on whose direction the adsorption takes place[14].

The rate of copper deposition is influenced by several factors, such as the kinetics of Cu^{2+} ions reduction, the electrochemical behaviour of organic compounds at the electrode interface and also how the flow of Cu^{2+} ions reaches the electrode surface[15]. It has been found that the adsorption of organic compounds at the interface leads to a decrease of the Cu^{2+} ions diffusion coefficient and of the mass transport rate[16] although Cu^{2+} diffusion mechanism remains the same.

The aim of this research is to study, the adding of vitamin C to the electrodeposition bath to improve the surface softness the brightness and the grain size of deposits and reduce dendritic formations.

EXPERIMENTAL

The bath solution ($CuSO_4.5H_2SO_4$) was placed into a single compartment of two-electrode cell. The electrodeposition experiments were performed using copper plate (10 cm × 5 cm × 0.2 cm) as cathode and anode. The copper used to have the following composition (Wt %): 0.0001 Cd, 0.001 Ag, 0.003P, 0.003 Pb, 0.005 Sn and Cu is 99.98. Current was supplied by DC power supplier model 34 B DCPS (Testronix). All the experiments were carried out at 20, 30, 40 and 50 ± 1 °C. The temperature of the bath remained almost constant during the experiments. The morphological analysis was performed by scanning electron microscope (SEM) (JEOL, JSM-5300, scanning microscope, OXFORD instrument). For this purpose the copper sheet cathode was (1 cm × 1 cm).

Preparation of solution: All chemicals were AnalaR grade and supplied by BDH chemicals Ltd. The concentration of vitamin C varied from 1×10^{-5} to 6×10^{-5} mol/L. The copper sulphate and sulfuric acid (98 % w/w) concentration were 0.1 and 0.5 M, respectively, for all experiments. Copper sulphate concentration was checked by iodometry[17]. The total volume of the electrolytic bath solution was made up to 300 mL. Doubly distilled de-ionized water with a measured resistivity > 18 mΩ was used in the preparation of solutions.

RESULTS AND DISCUSSION

Effect of sulphuric acid concentration: Fig. 1 and Table-1 compares the cathodic polarization curve of copper reduction in the deposition solution with different concentration of sulphuric acids 0.5, 1, 1.5, 2 and 2.5 M. The electrodeposition was carried was carried out at 20 °C. The curves show the typical I-V characteristics for electrodeposition. Initially, the current linearly increased from the beginning of potential scan and reaches a plateau. This behaviour is dominated by the ohmic resistance in the electrolyte. At high potential, fluctuation is both potential and current are found. Above the horizontal range, the current stays constant, even though the potential augments. The continued augment in potential lead to enlarge in current due to hydrogen evolution as shown in Fig. 1, there is a well defined region of these cathodic polarization curves, limiting current plateau, when cathodic polarization test was carried out in 0.5 M sulphuric acids.

Wider limiting current plateau is an advantage since it provides a wider operating window for electrodeposition process[18]. The broad limiting plateau is observed at 0.5 M sulphuric acids.

TABLE-1
VALUES OF LIMITING CURRENT OF COPPER ELECTROREFINING IN 0.1 M $CuSO_4$ + DIFFERENT CONCENTRATION OF H_2SO_4 AT 293 K

H_2SO_4 conc. (mol/L)	Cu–Cu				
	0.5	1.0	1.5	2.0	2.5
I_L (A)	0.283	0.253	0.232	0.192	0.152
i_L (A cm^{-2})	0.011	0.010	0.009	0.008	0.007

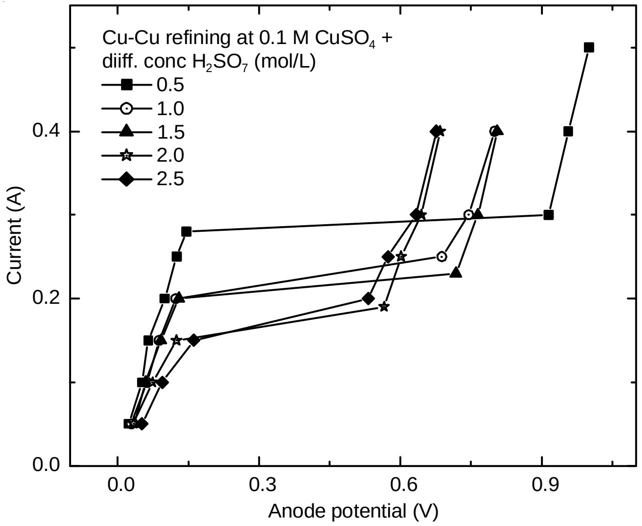

Fig. 1. Effect of different concentrations of H_2SO_4 on limiting current of copper refining

It was observed that as the sulfuric acid concentration reduces the limiting current amplify. The maximum limiting current is recorded for 0.5 M sulphuric acid. Throwing power increases dramatically in low-copper (0.10 M), high sulfuric acid solutions[18]. Excess sulfuric acid drastically increases the cathodic overpotential and introduces a smaller ratio of level plane of electrodeposits resulting in nodular precipitates[19].

In typical baths the high sulfuric acid concentration has a enormous bearing upon discharge kinetics as well as growth structure and morphology. This influence is generally attributed to specific adsorption of sulfate anion[20], diminished Cu^{2+} ions activity and increased concentration overpotential upon Cu^{2+} discharge. In addition, the surface concentration of H ions was shown to amplify considerably with H_2SO_4 concentration[21], suggestive of a specific manipulate of hydrogen surface coverage upon copper discharge kinetics. consistent with our results, elevated free acid content in the electrolyte has a dual influence: a kinetic hindrance related to small Cu^{2+} concentration at the surface and a little stability of discharge intermediates (Cu^+ ions), as incidental from values, that is, a speedy ionic discharge step. Lower acid content, down to 0.5 M, diminishes surface inhibition, slightly favouring intermediates accumulation at the surface.

Effect of vitamin C concentration: Polarization curves with a well-defined limiting current plateau Fig. 2 were obtained for the cathodic reduction of copper in the presence of different concentrations of vitamin C. The inhibition efficiency (IE) was calculated from polarization measurements according to the relation given below:

$$\text{IE}\ (\%) = \frac{I_{L(\text{blank})} - I_{L(\text{vitamin C})}}{I_{L(\text{blank})}} \times 100 \qquad (1)$$

where $(I_L)_{\text{blank}}$ and $(I_L)_{\text{vitamin C}}$ are the limiting currents determined by the intersection of the extrapolated lines and the deposition potential for the copper in blank and vitamin C containing acidic sulphate solution, respectively.

Fig. 2 and Table-2 review the results obtained and demonstrate that the limiting current reduces and inhibition efficiency (IE) amplifys by growing vitamin C concentrations. This drop

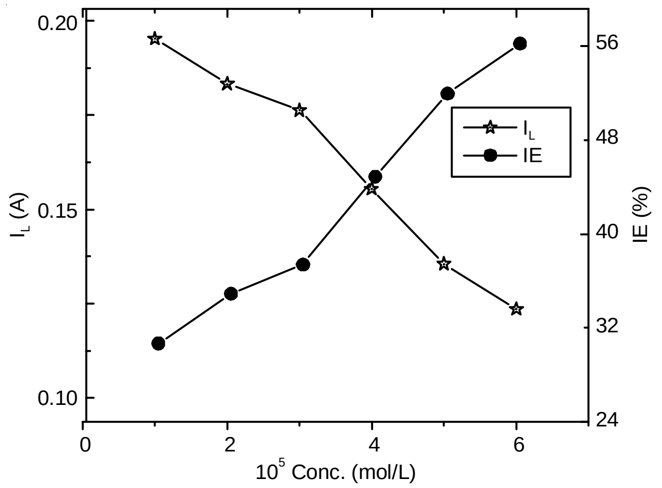

Fig. 2. Variation of limiting current, % inhibition, for the electrorefining of vertical copper by copper in 0.1 M $CuSO_4$ + 0.5 M H_2SO_4 with the concentration of ascorbic acid

TABLE-2
VALUES OF LIMITING CURRENT, % INHIBITION, FOR THE ELECTROREFING OF VERTICAL COPPER IN 0.1 M $CuSO_4$ + 0.5 M H_2SO_4 IN PRESENCE OF DIFFERENT CONCENTRATION OF ASCORBIC ACID AT 293 K

10^5 ascorbic acid conc.	0.00	1.0	2.0	3.0	4.0	5.0	6.0
I_L (A)	0.283	0.202	0.190	0.183	0.162	0.142	0.130
IE (%)	0.000	28.62	32.86	35.34	42.76	49.82	54.06

off in the limiting current may be due to organic additives adsorption to the electrode surface. The concentration of vitamin C molecules at the electrode solution boundary may augment the viscosity with a subsequent diminish in the diffusion of electro-active copper ions. The amplify in interracial viscosity and the port of the solution to the electrode surface by vitamin C molecules delay the run of the solution past the electrode surface with a resulting in reduce in the limiting current as well as by the possible creation of copper complexes in the partial space of the diffusion film where adsorbed ascorbic acid concentration is high and Cu^{2+} concentration is small[22,23].

Vitamin C has polycentric adsorption spots (including various O atoms). These uniqueness would afford the compounds the capability to adsorb on the metal/solution border *via* the electrostatic attraction between the charged metal and the charged addatives molecules, dipole-type interaction between unshared electron pairs in the compounds with the metal, π electrons-interaction with the metal and a mixture of all of the above[24]. With reference to ascorbic acid influence, a possible explanation must take into account the chemical interactions among ascorbic acid, metal ion and anions at the electrode. Ascorbic acid creates a analogous surface blocking result if added to both starting electrolytes, *via* the development of an adsorbed blockade at the electrode and reduction of the accessible active area. In the case of the typical bath the adsorbed blockade at the electrode is simply a mechanical impediment in opposition to copper ion transfer[25-27]. Refining additives were reported to increase the Cu level in the sulfuric acid bath and a similar effect could be induced by ascorbic acid[28]. Ascorbic acid addition, exhibits the unusual influence, the stable complex formation between ascorbic acid and Cu ions was already investigated by Hill and Rogers[28], alike to the case of cyclic polyether complexes with metal salts[29], giving molecular adducts between Cu^{2+} and ascorbic acid, which proceed as an electron pair donor through its oxygen atoms. Complex formation could be favoured by both high copper concentration and pH, a possible consequence of slightly weaker cation-solvent and ascorbic acid-solvent interactions.

Effect of temperature: It can be seen from Table-3 that increasing the temperature (20-50 °C) leads to an amplify of the limiting diffusion current in the absence and presence of 5 × 10^{-5} mol/L investigating vitamin C (ascorbic acid). This can be clarified in the next approach:

In the well-known Nernst limiting current density equation:

$$jL = nFDc_0/\delta \tag{2}$$

where nF is the number of Faradays per mole of consuming ions, c_0 is the concentration of Cu(II) ions, D is the diffusion coefficient and δ the thickness of the diffusion layer, a change in the temperature of the solution affects both D and δ. Modifiers of these changeables are affected by the well-known fact concerning the change of the viscosity of a solution by changing temperature.

The increase of temperature of electrolysis directs to an amplification of hydrogen evolution reaction[30]. Meanwhile, despite the intensification of hydrogen evolution with the rising temperature, the decrease in the number of cracks formed per mm^2 surface area of electrodes and the increase of their average diameter was observed during copper electrodeposition at an overpotential of 600 mV. In order to explain this unexpected trend in the development of morphology of electrodeposited copper, the effect of temperature on some properties of electrorefining solution, such as viscosity and surface tension was considered[31]. The increase of temperature causes the decrease of both the viscosity[32] and the surface tension of this solution[33]. The decrease of the surface tension of the solution lowers the break-off diameter of the hydrogen bubble from the electrode surface, while the reduced viscosity of the solution probably assists convey of the separated hydrogen bubbles through the interior of the deposit forming the channel structure through it. In any case, growing temperature led to reorganization of developed hydrogen from those generate honeycomb-like structure to structure with dominant presence of agglomerates of copper granule encircled by uneven channels of developed hydrogen (that is a channel structure).

Fig. 3 showed that as temperature increase, a decrease in the inhibition efficiencies (I.E. %) were clear, which indicates the formation of adsorptive film of a physical character[34].

Arrhenius plot for the deposition process of Cu is represented in Fig. 4. The activation energies can be calculated from the following set of equations:

$$I_L = K\exp(-E_a/RT) \tag{3}$$

$$I'_L = K\exp(-E'_a/RT) \tag{4}$$

where E_a and E'_a are the activation energies in the absence and presence of the ascorbic acid, respectively. T is the absolute temperature, K is the Arrhenius pre-exponential constant and R is the universal gas constant. The calculated values of

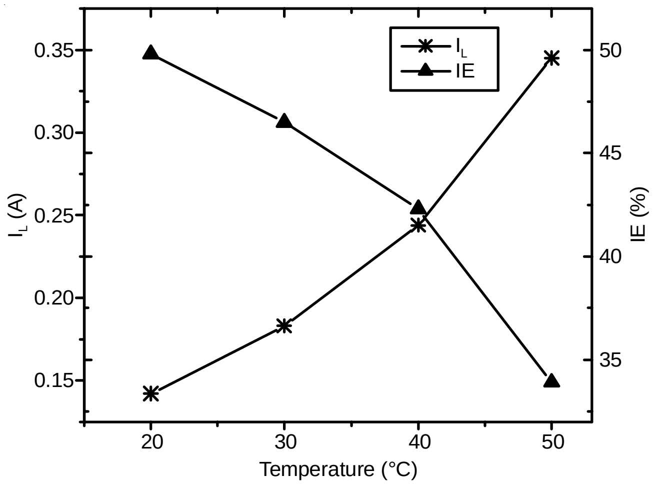

Fig. 3. Variation of limiting current, % inhibition, for the electrorefining of vertical copper by copper in 0.1 M $CuSO_4$ + 0.5 M H_2SO_4 with temperature in presence of 5 × 10^{-5} mol/L vitamins C.

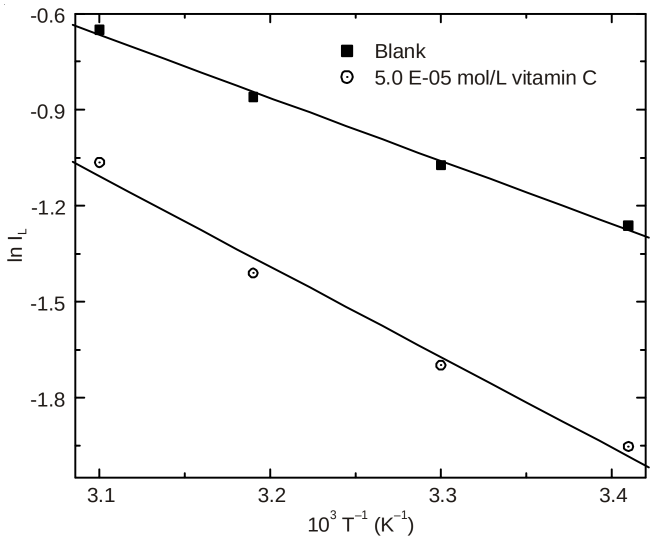

Fig. 4. Arrhenius plot of copper refining in the presence of 5 × 10^{-5} Mol/L vitamin C

apparent activation energy are: E_a =16.11 kJmol^{-1} and E'_a = 23.17 kJ mol^{-1}.

The results clearly show that the vitamin C containing solution has higher value of E_a than the free solution. The enhancement of E_a in the presence of the vitamin C designates that additional energy barrier for the deposition reaction in the presence of vitamin C is attained[35].

The growing in activation energy value in comparison to the blank solution, is generally interpreted as an sign for the formation of an adsorptive film. This fact is governed by a physical (electrostatic) mechanism or a weak chemical bonding between the inhibitor molecules and the metal surface[36,37].

The thermodynamic activated functions were obtained by applying the transition-state and Gibbs-Helmholtz equations:

$$I_L = (RT/Nh)\exp(\Delta S^{\#}/R)\exp(-\Delta H^{\#}/RT) \quad (5)$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \quad (6)$$

where $\Delta H^{\#}$ is the enthalpy of activation, $\Delta S^{\#}$ is the entropy of activation, $\Delta G^{\#}$ is the free energy of activation, h is Planck's constant and N is the Avogadro's number.

It is also noticed that elevated values of $\Delta H^{\#}$ in the existence of vitamin C comparing to value of $\Delta H^{\#}$ for free acidic solution (Table-3). The increase of activation enthalpy in the case of Vitamin C implies that the addition of Vitamin C increases the height of the energy barrier of the deposition reaction to an extent[38].

The values of $\Delta S^{\#}$ are larger and negative both in the absence and presence of vitamin C which implies that the activated complex in the rate determining step represents an association rather than dissociation step meaning that a reduce in disarray takes place on going from reactants to the activated complex

The weak dependence of $\Delta G^{\#}$ on the composition of vitamin C can be attributed largely to the general linear compensation between $\Delta H^{\#}$ and $\Delta S^{\#}$ for the given temperature[39].

Adsorption isotherm: The effectiveness of organic compounds as deposition inhibitors can be ascribed to the adsorption of molecules of vitamins C through their polar function on the metal surface.

Adsorption can affect the deposition rate in two possible ways[40]: In the first way, additives reduce the accessible reaction area through adsorption on the metal which is called geometric blocking effect. In the second way, additives adapt the activation energy of the cathodic reactions occurring in the additives –free metal in the course of the hindered deposition process which is called energy. It is a complicated task to decide which aspects of the retarding effect are connected to the geometric blocking action and which are attached to the energy effect. The metal surface in aqueous solution is always wraped with adsorbed water dipoles. Therefore, the adsorption of ascorbic acid from aqueous solution is a quasi substitution process[41].

$$\theta = \frac{I_{L(blank)} - I_{L(A.A)}}{I_{L(blank)}} \quad (7)$$

$$C/\theta = 1/K_{ads} + C \quad (8)$$

TABLE-3
VALUES OF LIMITING CURRENT FOR REFINING OF VERTICAL COPPER PLATE BY COPPER PLATE 0.1 M $CuSO_4$ + 0.5 M H_2SO_4 IN ABSENCE AND PRESENCE OF 5 × 10^{-5} mol/L VITAMINS C AT DIFFERENT TEMPERATURES AND ACTIVATED PARAMETERS FOR PROCESS

Temperature (°C)	20		30		40		50	
Ascorbic acid conc. (mol/L)	I_L (A)	I.E. %	I_L (A)	I.E. %	I_L (A)	I.E. %	I_L (A)	I.E. %
0.00	0.283	-	0.342	-	0.423	-	0.522	-
5 × 10^{-5}	0.142	49.82	0.183	46.49	0.244	42.31	0.345	33.90
Activated parameters	E_a (kJ mol^{-1})		$\Delta H^{\neq}$ (kJ mol^{-1})		$-\Delta S^{\neq}$ (J mol^{-1} K^{-1})		$\Delta G^{\neq}$ (kJ mol^{-1})	
0.00	16.11		13.64		200.04		75.91	
5 × 10^{-5}	23.17		20.69		190.63		77.53	

The surface coverage (θ) data are very helpful while discussing the adsorption characteristics, when the portion of surface covered is calculated as a function of the concentration at constant temperature, adsorption isotherm could be estimated at equilibrium condition. The reliance of the portion of the surface covered area (θ) on the concentration (C) of the vitamin C was investigated graphically by fitting it to Langmuir isotherm[42]. Fig. 5a demonstrates linear plot for C/θ *versus* C with $R^2 = 0.997$ correlation coefficient, but the slope illustrate departure from the value of unity (1.45) as would expected for the ideal Langmuir isotherm equation. This deviation from unity may be due to the interaction between the adsorbed species on metal surface. The Langmuir isotherm equation is based on the assumption that solid surface contains a fixed number of adsorption sites holds one adsorbed species and don't interact with one another, but this is not true in case of Vitamin C which having polar atoms which adsorbed on the active sites of the metal[43].

Recent researches have looked into the action of additives from a purely mechanical kinetic point of view. This relation can be stated as Okafor *et al.*[44] kinetic thermodynamic adsorption model (Fig. 5b). The model may be formulated as

$$\log (\theta/1\text{-}\theta) = \log K' + y\log C \qquad (9)$$

where y is the number of inhibitory molecules occupying one active site. Value of y greater than one entail the pattern of multilayer of the inhibitor on the metal surface. However, the values of y less than one indicate that vitamin C will engage more than one active site. K_2 is a constant related to the binding constant of adsorption process K by the following relationship[19].

$$K = K_2^{(1/Y)} \qquad (10)$$

The efficiency of a given vitamin C is a function of both the scale of its binding constant K and the number of active sites (1/y) it is capable of blocking with the former being the most significant. A great value of K revenue better and strong interaction, while slighter values of K denote that the interaction between the ascorbic acid molecules and the copper metal is feebleer. Hence, consistent with the mathematical value of K obtained (17.18×10^3), the prevalent value of K recorded for ascorbic acids, designate brawny interaction. The value of 1/y obtained mostly greater than one ($1/y > 1.67$). This implies that a given ascorbic acid molecule will engage more than one active site on the copper surface[45].

K is related to the free energy of adsorption ΔG_{ads} by the equation:

$$\Delta G_{ads} = -RT \ln (55.5\ K) \qquad (11)$$

where R is the universal gas constant, T is the absolute temperature and the value of 55.5 is the concentration of water in the solution. The negative values of ΔG_{ads} calculated from eqn. 11 imply that the adsorption of vitamin C is allowed from thermodynamic point of view and indicates spontaneity of the adsorption process and the stability of the adsorbed layer on the copper surface. Generally, the energy values of -20 kJ/mol or less negative are reliable with an electrostatic interaction between the charged molecules and the charged metal (physisorption) while those more negative than 40 kJ/mol are associated with chemisorptions which consequences of a sharing or transfer of electrons from the additives molecules to metal surface to from a coordinate covalent bond. In the present work, the calculated value -33.54, less than the threshold value (-40 kJ/mol) required for chemical adsorption and IE % decreases with increase in temperature. These sustain the mechanism of physical adsorption[41].

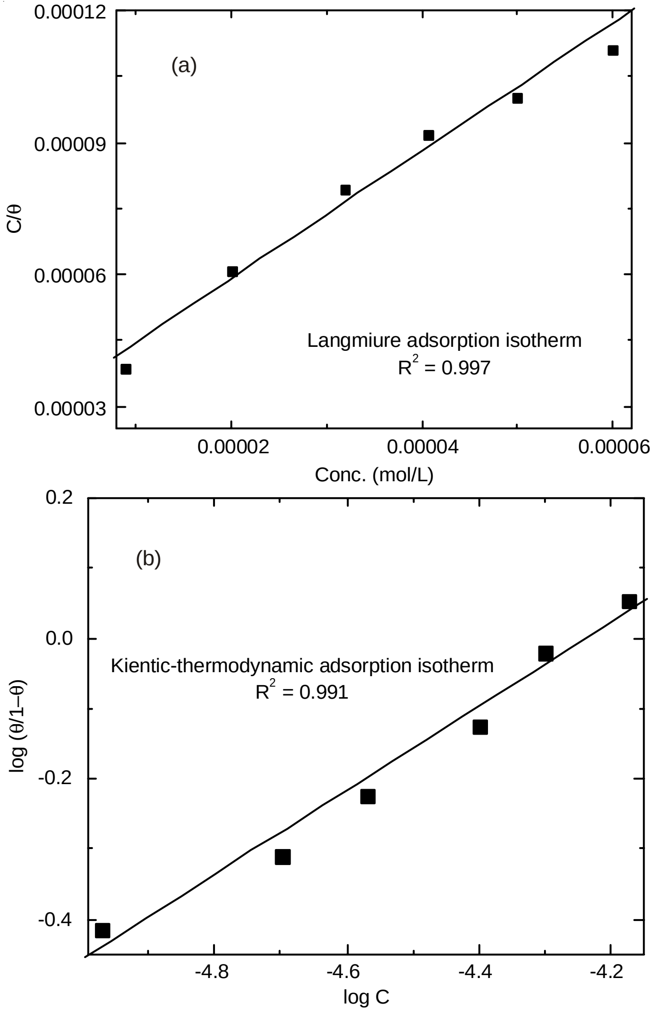

Fig. 5. Thermodynamic adsorption isotherm vitamin C at 20 °C (a) Langmuir (b) Kientic

Surface characterization (scanning electron microscope): In order to study the role of vitamin C in the electrorefining of Cu, the surface morphology of copper samples immersed in a bath of (0.1 M $CuSO_4 \cdot 5H_2O$, 0.5 M H_2SO_4) with or without additives was widely studied. All trials were made at the limiting current resolved for all solutions at 20 °C, pH =1.8 and time of 5 min. The morphologies of the copper deposits obtained under described hydrogen co-deposition conditions are presented in Fig. 6(a). Analysis of these twigs at the micro level revealed that the twigs consisted of agglomerates of copper grains. It's a porous, canal structure through which the interior of the powder particle can be seen. These canals were generated *in situ* by the simultaneous processes of the formation of copper particles. Addition of vitamin C (Figs. 6b and 6c) to copper bath exhibits a strong influence on the microstructure *i.e.* refining the deposit. The cumulative are rounded and grain size is smaller forming a monolayer on the copper surface because they are powerfully adsorbed on copper

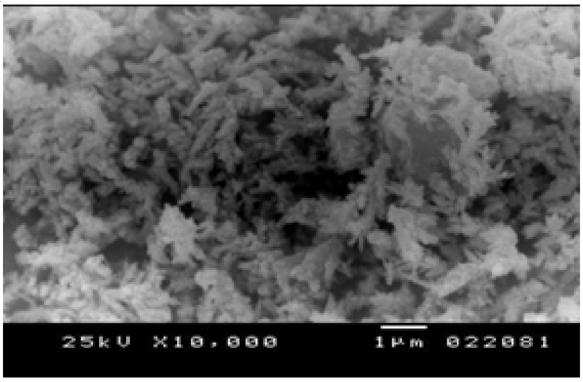

Fig. 6a. Blank of copper

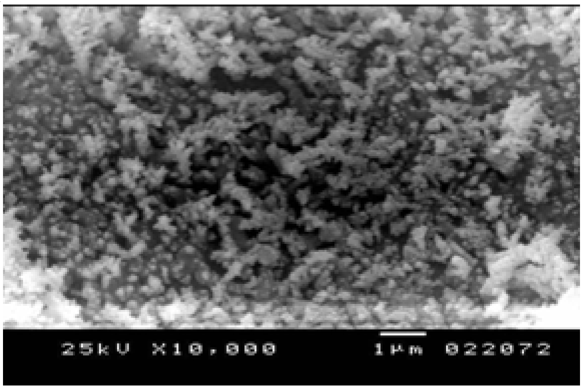

Fig. 6b. After ER + 2 × 10^{-5} M vitamin C

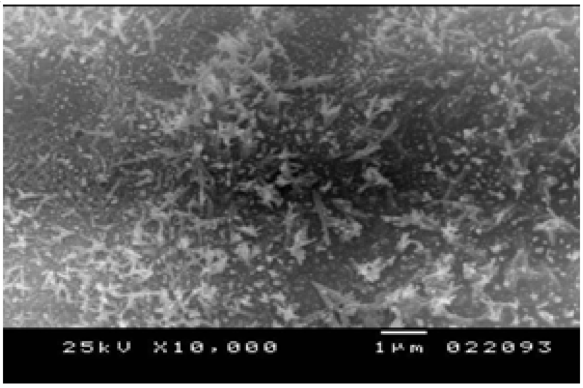

Fig. 6c. After ER + 6 × 10^{-5} M vitamin C

blocking the active sites for electrodeposition. Finally, it modifies the nucleation mechanism and slow downs crystal growth process. The result is visible in the properties of the coating which is even and brilliant with slight roughness. At low concentration of vitamin C , the deposit is less uniform and slightly rough but by increasing the concentration the deposited organic substituents is powerfully advocate and uniformly covers the entire electrode surface.

The addition of vitamin C to bath strongly modifies the growth characteristics and the crystal habit: faceted grains with twinning appear at the surface, resulting from the aggregation of very fine particles. Vitamin C addition to bath completely suppresses the preferential growth of isolated crystal, providing a self-evident picture of its strong inhibiting action. As a consequence, modifying grain morphology through formation of smooth, flat, uniform facets of relatively large extent, maintaining the same grain size. In these conditions, growth is under nucleation control through adsorption of dischargeable species, destabilising the base reproduction growth mode. Surface blocking leads to the development of a featureless morphology, with complete suppression of preferential growth of isolated crystals in the early stages of deposition, promoting structure refinement and surface leveling.

Cathodic current efficiency of electrodeposition (CED) and energy consumpustion: During the passage of one Faraday of current electrodeposition, electrorefinning of copper and electrolysis of water occur. CED of copper was determined by mass increase of the copper cathode. Based on the current used for the particular period of electrolysis, the theoretically expected weight of copper deposition was calculated using Faraday's law:

$$W = Z\,I\,t \tag{12}$$

where: W, Z, I and t are theoretically expected mass of copper deposit, electrochemical equivalent of copper, current in A, time in s, respectively. CED is calculated using the relation:

$$CED = (w/W) \times 100 \tag{13}$$

where: w = the mass of copper deposited on cathode during experiment. The data are presented in Table-4. It was found that the CED incease by increasing vitamin C concentration (Table-4).

Table-4 shows the effect of vitamin C on the cell voltage and on the electrical power consumption (EPC; in kWh/kg) of copper ions reduced at the cathodic limiting current. Electrical power consumption was calculated from the formula:

$$EPC = EIL/1000 \times m \tag{14}$$

where E is the cell voltage at the limiting current, m is the amount of Cu^{2+} reduced (as Cu) at the cathode in kilograms per hour. It was calculated from Faraday's law m = eI t/1000, where e is the electrochemical equivalent, e = 63.5/2 × 96500 g/Coulomb and t is the electrolysis time in seconds.

Table-4 shows that the cell voltage and electrical power consumption reduce with augment in concentration of vitamin C. This decrease in cell voltage and electrical power spending is attributed mostly to reduce in ohmic drop of the cell (IR drop) as a result of decreasing the limiting current due to adding vitamin C.

TABLE-4
EFFECT OF VITAMIN C ON THE CELL VOLTAGE AND ELECTRICAL POWER CONSUMPTION AT THE LIMITING CURRENT OF THE ELECTROREFINING

10^{5} ascorbic acid conc. (mol/L)	0.00	1.0	2.0	3.0	4.0	5.0	6.0
I_L (A)	0.283	0.202	0.190	0.183	0.162	0.142	0.130
w	0.0148	0.0110	0.0106	0.0103	0.0092	0.0081	0.0075
W	0.0167	0.0119	0.01125	0.0108	0.0096	0.0084	0.0077
CED	88.62	92.43	94.22	95.37	95.93	96.42	97.40
Cell voltage (V)	0.445	0.440	0.435	0.430	0.425	0.420	0.412
10^5 Electrical power (kWh/kg)	7.78	7.70	7.60	7.52	7.43	7.35	7.21

Conclusions

- As the sulfuric acid concentration reduce the limiting current amplify.
- Vitamin C is a suppresser with the strongest action on copper electrodeposition and inhibition efficiency growing by rising vitamin C concentration.
- As the temperature raise, a diminish in the inhibition efficiencies (IE) %) were monitored, which designates a physical adsorptive nature.
- The adsorption of vitamin C on cathode copper surface follow Kinetic-thermodynamic adsorption isotherm.
- The addition of vitamin C to bath strongly modifies the growth characteristics and the crystal tradition.
- Current efficiency augments and energy consumption diminishs of copper electrodeposition as vitamin C concentration increase.

REFERENCES

1. M.A. Pasquale, L.M. Gassa and A.J. Arvia, *Electrochim. Acta*, **53**, 5891 (2008).
2. L.D. Burke and R. Sharna, *J. Electrochem. Soc.*, **155**, 285 (2008).
3. M.S. Kang, S.-K. Kim, K. Kim and J.J. Kim, *Thin Solid Films*, **516**, 3761 (2008).
4. D.R. Turner and G.R. Johnson, *J. Electrochem. Soc.*, **109**, 798 (1962).
5. B. Bozzini, L. D'Urzo and C. Mele, *Electrochim. Acta*, **52**, 4767 (2007).
6. A.L. Portela, M.L. Teijelo and G.I. Lacconi, *Electrochim. Acta*, **51**, 3261 (2006).
7. C. Firoiu, Tehnologia Proceselor Electrochimice, Ed. Didactica si Pedagogica, Bucuresti (1983).
8. N. Ibl and K. Schadegg, *J. Electrochem. Soc.*, **114**, 1268 (1967).
9. C.C .Vaduva, N .Vaszilcsin and A. Kellenberger, The Annals of Dunarea de Jos University, Fascicle IX, Metallurgy and Mineral Science, pp. 180-187 (2011).
10. A. Milchev and T. Zapryanova, *Electrochim. Acta*, **51**, 2926 (2006).
11. C.C. Vaduva, N. Vaszilcsin, A. Kellenberger and M. Medeleanu, *Int. J. Hydrogen Energy*, **36**, 6994 (2011).
12. C.C. Vaduva, C.N. Vaszilcsin and A. Kellenberger, *Corros. Anticorros. Protect.*, **6**, 23 (2011).
13. C.C. Vaduva, C.N. Vaszilcsin, A. Kellenberger and B.I. Pancan, *Corros. Anticorros. Protect*, **6**, 19 (2011).
14. O.L. Blajiev, T. Breugelmans, R. Pintelon, H. Terryn and A. Hubin, *Electrochim. Acta*, **53**, 7451 (2008).
15. L. Gavrila, Fenomene de Transfer, Alma Mater, Bacau, vol. II (2000).
16. H.H. Abdel-Rahman, A.M. Ahmed, A.A. Harfoush and A.H.E. Moustafa, *Hydrometallurgy*, **104**, 169 (2010).
17. J. Mendham, R.C. Denney and M.B. Thomas, Vogel's Quantitative Chemical Analysis, edn 6 (2004).
18. B.F. Rothschild, *Plating Surf. Finish.*, **66**, 70 (1979).
19. Y. Fukunaka, H. Doi, Y. Nakamura and Y. Kondo, in eds.: L.T. Romankiw and T. Osaka, Electrochemical Technology in Electronics, Electrochemical Society, Pennington, NJ, Vol. 88-23, p. 83 (1988).
20. W.D. Barba and T. Hurlen, *J. Electroanal. Chem.*, **91**, 359 (1978).
21. K. Denpo, T. Okumara, Y. Fukunaka and Y. Kondo, *J. Electrochem. Soc.*, **132**, 1145 (1985).
22. A.A.J. Taha, *Colloids Interf. Sci.*, **275**, 235 (2004).
23. A. Gomes and M.I. da Silva Pereira, *Electrochim. Acta*, **52**, 863 (2006).
24. A.M. Abdel-Gaber, B.A. Abd-El-Nabey, I.M. Sidahmed, A.M. El-Zayady and M. Saadawy, *Corros. Sci.*, **48**, 2765 (2006).
25. W. Plieth, *Electrochim. Acta*, **37**, 2115 (1992).
26. J.D. Reid and A.P. David, *Plating Surf. Finish.*, **74**, 66 (1987).
27. L. Mirkova, St. Rashkov and C. Nanev, *Surf. Technol.*, **15**, 181 (1985).
28. M. Hill and G.T. Rogers, *J. Electroanal. Chem.*, **86**, 179 (1978).
29. A. Vicenzo and P.L. Cavallotti, *J. Appl. Electrochem.*, **32**, 743 (2002).
30. N.D. Nikolic, L.J. Pavlovic, M.G. Pavlovic and K. Popov, *J. Serb. Chem. Soc.*, **72**, 1369 (2007).
31. A. Amadi, D.R. Gabe and M. Goodenough, *J. Appl. Electrochem.*, **21**, 1114 (1991).
32. H. Vogt and R.J. Balzer, *Electrochim. Acta*, **50**, 2073 (2005).
33. A.M. Al-Sabagh, H.M. Abd-El-Bary, R.A. El-Ghazawy, M.R. Mishrif and B.M. Hussein, *Egypt. J. Petrol.*, **20**, 33 (2011).
34. M.A. Deyab, *Corros. Sci.*, **49**, 2315 (2007).
35. M. Bouklah, N. Benchat, A. Aouniti, B. Hammouti, M. Benkaddour, M. Lagre'nee, H. Vezin and F. Bentiss, *Prog. Org. Coat.*, **51**, 118 (2004).
36. F. Kellou-Kerkouche, A. Benchettara and S. Amara, *Mater. Chem. Phys.*, **110**, 26 (2008).
37. S.S. Al-Juaid, *Portug. Electrochim. Acta*, **25**, 363 (2007).
38. Z. Tao, S. Zhang, W. Li and B. Hou, *Corros. Sci.*, **51**, 2588 (2009).
39. O.L. Riggs Jr, Corrosion Inhibitors, in ed.: C.C. Nathan, NACE, Houston, TX, edn 2 (1973).
40. A. Hamdy and N.S. El-Gendy, *Egypt. J. Petrol.*, **22**, 17 (2013).
41. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
42. D. Prabhu and P. Rao, *J. Environ. Chem. Eng.*, **1**, 676 (2013).
43. A.A. El-Awady, B.A. Abd-El-Nabey and S.G. Aziz, *J. Electrochem. Soc.*, **139**, 2149 (1992).
44. I.E. Uwah, P.C. Okafor and V.E. Ebiekpe, *Arabian J. Chem.*, **6**, 285 (2013).
45. A.R.S. Priya, V.S. Muralidharam and A. Subranania, *Corrosion*, **64**, 541 (2008).