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Optimal Conditions for Electrodeposition of Copper (II) in Presence of Alizarin Red's by Physicochemical Methods

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Abstract

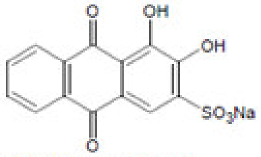
The comprehensive physical properties of the aqueous solutions of (alizarin red S - copper(II) chloride) were studied in this research with fixing the conditions (pH – concentration – temperature), then the optimal conditions for the formation of the complex Copper(II) – Alizarin Red S (ARS – Cu II) were appointed by several ways: (the pH measurement method - electrical conductivity measurement method – UV/Vis spectral method), and then the stoichiometry of the reaction of the complex formation was determined by three reference methods. It found that the complex formed when each concentrations greater than a certain limit (10^{-5} M). In addition, the complex could formed at higher concentrations by adjusting the (pH) at a suitable value (4.2 → 5.8). Finally, the complex remains stable with the time keeping at suitable conditions (a way from the sun light and a way from a high temperature). Also, the electrodeposition of copper(II) was studied to determine the appropriate operating conditions and the thicknesses of the coating layer. It was obtained a good properties (brightness - surface covering: distribution of atoms - thickness .... etc.). of deposit without using of any other additives by applying the conditions (pH = 5, i = 2 mA/cm^2, t = 5 min, C = 0.1 M $\Rightarrow$ d = 1.756×10^{-5} cm).

Keywords: Alizarin red S - (ARS – Cu II) complex - electrodeposition of Cu (II).

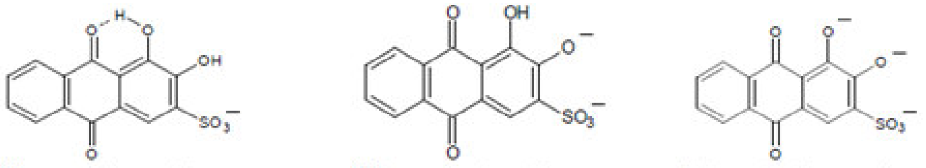
Introduction

Copper is an excellent choice for an underplate, since it often covers minor imperfections in the base metal. It is relatively inert in most plating solutions of other common metals; it has a very high plating efficiency, resulting in excellent coverage even on difficult-to-plate parts; and lastly, it is highly conductive, making it an excellent coating for printed wiring boards or as a coating on steel wire used to conduct electricity [i]. At the present time only the sulfate and fluoborate solutions are commercially used.

On the other hand, the complexes are good organizers for the deposition process. Among the anthraquinone dyes, Alizarin and its derivatives are well known colorimetric reagents. Alizarin Red S (ARS; 1,2-dihydroxy 3-anthraquinone sulphonic acid) has found application in the micro determination of a number of metals [ii]. The presence of a quinoid oxygen, with two hydroxyl groups at - and - positions in ARS, makes it very suitable for chelation. Coordination bonding of metal to dye molecule occurs when phenolic group of dye is partly oxidized and partly ionized and metal gets bound. Oxidized quinonic oxygen begins to form a coordination with the same metal and thus chelate is formed which facilitates the charge transfer (CT) from ligand to metal ion, which is responsible for its chromophoric properties. This property has been exploited in the detection and determination of a number of transition metals [iii]. The electrochemical behavior of ARS has been also studied in connection with voltametric determination of metals like Ca, Sc and Al [iv, v]. The presence of sulphonate group in the molecule adds further reactivity to the molecule. The sodium salt of the dye has structure (i) (Scheme-1) which takes different forms in different media (ii-iv) (Scheme-1):



(i) Alizarin Red S



(ii) In acidic medium (iii) In neutral medium (iv) In alkaline medium

Scheme(1): Deferent formula of (ARS) in variable meduim.

Cordeiro et al. have studied ARS as a coordination ligand electrode surface to facilitate Cu(II) preconcentration process by absorptive stripping voltammetry [vi].

Experimental

Apparatus and chemicals

UV/Vis spectroscopy (model: Optizen 2120 UV), pH and Electrical Conductivity Measure (GONDO) (Model: PL-700PC), External Current Resource (PROMAX) (Model: FUENTE DE ALIMENTACION FAC-662B), Resistors Tray, Connecting Wires, volt-amp Measure (Model: M890C$^+$), Bath Coating with (anode electrode which was made of a paste of graphite and paraffin oil) (made in the laboratory), Bath Coating with soluble anodes of sheets of copper, Bath Coating with insoluble dry anodes of graphite, Cylindrical Cathodes which was made of industrial iron (steel), Cylindrical Stainless Steel Cathodes which had a national commercial code (405). $CuCl_2.2H_2O$, CH_3COONa, ARS and NaOH from Sigma-Aldrich and Merck with reagent grade.

Experimental Procedure:

1 – pH metric and electrical conductivity methods

(25ml) of different percentage of ($CuCl_2$ and ARS) mixtures with an initial concentration (0.004M) for each compound were titrated with [NaOH (0.01M)] solution by conductivity and pH methods. Those concentrations have been adopted in all subsequent work steps unless it was noted, and double distilled water has been used. The appropriate conditions for the formation of the complex were also identified by conductivity method using (9ml ARS + 3ml $CuCl_2$) mixture and adding [22.5ml (CH_3COOH + CH_3COONa). pH = 5] solution to adjust the pH value. The mixtures had been studied priory without adding the buffer solution, and measuring pH and conductivity for each combination, by consequent, any results were not conclude acceptable comparing with the results of the later experiments in this research which took acidity into account. In addition, the reaction stoichiometry was determined by taking (12ml ARS + 12ml buffer. pH = 5) solution and adding (24ml $CuCl_2$) to have the same optimum concentration, where in each batch has been added (1ml) as a way for (ARS) solution titration by measuring the conductivity.

2 - Spectrophotometric method:

Several experiments was performed by using of (Cu^{2+} + ARS^-) mixtures, where its used initial concentration was (0.004M) for each initial solution, then the optimum conditions to form the complex were determined by adding the buffer solution to the mixtures and noting form of the spectrum characteristic of the complex at the optimal conditions. Later experiments were carried out to determine the correct reaction stoichiometry at the optimum conditions.

3 - Electroplating of copper(II) experimentally:

An (1L) plastic bath was used, the inside of the bath was coated by graphite paste to use as anode (thickness = 1mm), cylindrical-shape industrial iron (Steel) and stainless steel, which had a national commercial code (405), were used as cathode to realize the coating process. Also, 0.5L glass bath was used as coating bath, and other two types of cathodes were used (insoluble solid cathodes of graphite and soluble cathodes of copper).

Deposition processes were done in each experiment as the following steps:

1- (0.004M, 1L) ($CuCl_2.2H_2O$) solution was prepared; 250ml were used for every bath coating.

2- (0.004M, 1L) (ARS) solution was prepared; 250ml were used for every bath coating.

3- 250 ml of prepared solution in 1 and 250 ml of prepared solution in 2 were mixed and 250 ml of the acetate buffer solution to adjust the (pH) value for each bath solution. The total volume of solution equal (750 ml).

4- Cathode (stainless steel or steel) was cleaned by (6×10^{-3}M) NaOH solution for 10min to remove fatty material, then was washed for 2min in double distilled water. Finally, the cathode surface was washed for 5min in (0.1M) HCl.

5- The surface of cathode was activated by immersing in (0.02M) H_2SO_4 for 1min, then washed it several times by a double distilled water to have the effective textured surface

6- The prepared cathode was weighed, immersed in the bath for depth (4cm) where stainless steel cathode diameter is (10mm) and for steel is (8mm).

7- The electrical circuit was closed to start the coating process at a certain voltage and current density and specific time without stirring the solution.

8- The coated cathode was washed after the end of the experiment by double distilled water, then was dried by methanol, finally was weighed quickly to avoid the oxidation reactions, and calculated the current efficiency and coating film thickness.

4 - Steps of calculations performance:

*- Current efficiency was calculated in each experiment from the following equation [vii]:

$$BT\,\% = \frac{M_M}{Q.I.t}\times 100$$

Where M_M: is deposited metal weight on the cathode (g), where the cathode was dried and weighed carefully before and after the coating process.

Q = (M/zF): is electrochemical equivalent which equal to (1.185 g/Ah) for copper.

M: atomic mass of the metal deposited, F = 26.8 Ah, z = 2.

I: current intensity (A). t: electrolysis time (h).
*- Formed coating film thickness was calculated from the following equation [viii]:

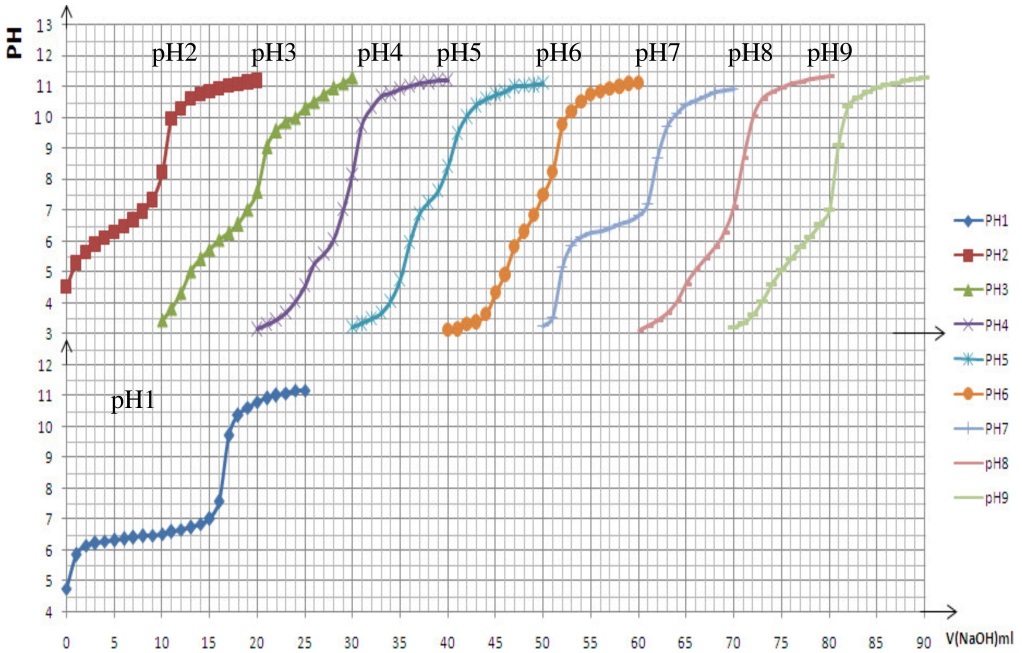
$$d = \frac{M_M}{\rho .\ S}$$

Where ρ: is the density of the deposited metal on the cathode which is equal to (8,96 g/cm^3) of copper, and S: is the coated surface area which is equal to (13,35cm^2).

Results and Discussion

1 - pH-metery method:

Samples have been titrated versus (0.01M) sodium hydroxide solution, and the following curves were obtained:



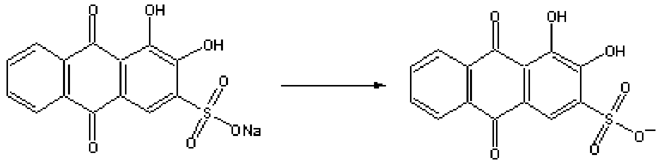
Figure(1): ***pH1***: titrated (25ml) ($CuCl_2.2H_2O$) ($4x10^{-3}$M) solution curve. ***pH2***: titrated (25ml) (ARS) ($4x10^{-3}$M) solution curve. ***pH3***: titrated (1:4) (5ml $CuCl_2$+20ml ARS) mixture solution curve. ***pH4***: titrated (1:1.5) (10ml $CuCl_2$+15ml ARS) mixture solution curve. ***pH5***: titrated (1:1) (12.5ml $CuCl_2$+12.5ml ARS) mixture solution curve. ***pH6***: titrated (1.5:1) (15ml $CuCl_2$+10ml ARS) mixture solution curve. ***pH7***: titrated (4:1) (20ml $CuCl_2$+5ml ARS) mixture solution curve. ***pH8***: titrated (1:2) (8.3333ml $CuCl_2$+16.6666ml ARS) mixture solution curve. ***pH9***: titrated (1:3) (6.25ml $CuCl_2$+18.75ml ARS) mixture solution curve. *the volume of (NaOH) is calculated for (**pH3** → **pH9**) curves by reducing the (10) value and its multiples for each curve in a row and for each taken point.*

The curve (***pH1***, metal salt solution) shows a large acid region of metal salt solution before the equivalence point, where the (Cl^-) ion liberates partially in the solution as in next equations (A, B), and titration process shifts the equilibrium continuously toward the full displacement until the end of titration [ix]:

$Cu^{2+} + Cl^- \leftrightharpoons CuCl^+$ log β = 1.03 ± 0.03 (A)

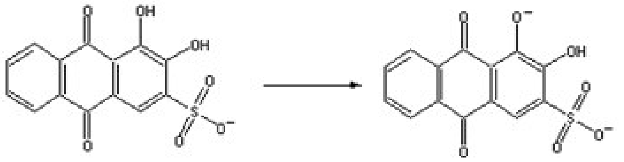
$Cu^{2+} + 2Cl^- \leftrightharpoons CuCl_2$ log β = 1.6 ± 0.07 (B)

As can be seen from the curve (***pH2***, reagent solution), when adding (1ml) of (NaOH) solution, a region buffer is formed, and still keeping that until adding (9ml) of (NaOH). So, it is due to the weak acidity of reagent, where the first (-OH) group of the reagent is started to titrate in this medium, and this is what corresponds to the reference that the study referred to in the introduction of this research, where the reagent is displaced in water according to the following interaction [x-xi]:



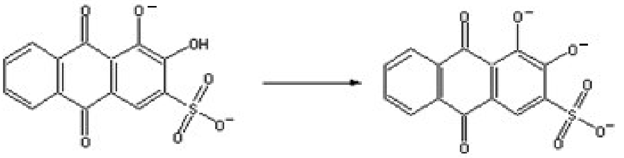
pKa = 0.97 ------(C)

When the solution approaches to the neutral medium and that when adding a little alkali solution, the displacement of the first (-OH) group is according to the following reaction:



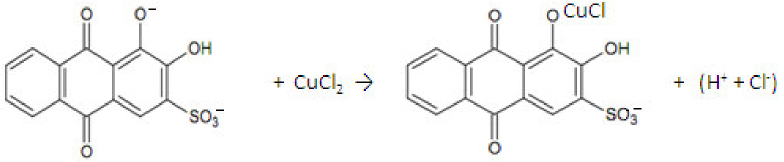
pKa = 6.17 ------(D)

As for when titration is accessed to the equivalence point of the second (-OH) group, the reagent displacement in alkaline media is according to the following reaction:



pKa = 11.36 ------(E)

[***pH3***, (5ml $CuCl_2$+20ml ARS) solution] curve shows the low pH of solution to approximately (3.3), it is due probably to the fact that both of reagent and metal ions solutions have two pH values close to the neutral medium which the reagent molecules be partly displaced, therefore are bonded with ($CuCl^+$) ions and ($H^+ + Cl^-$) forms as a byproduct in the solution, since the additions alkali solution before reaching the second equivalence point is consumed for the first (-OH) group titration of the remaining non-linked reagent, and also consumed to titrate the hydrochloric acid resulting from the expected following interaction:



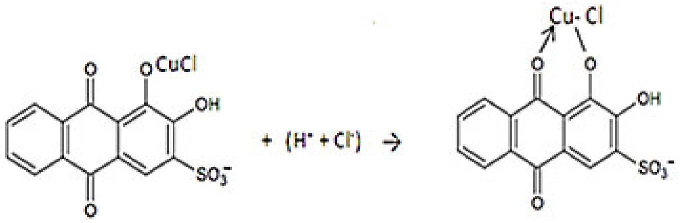
------ (1)

The evidence of the salt form which was described in the products of the previous reaction is the forming of a new product color, which is violet, in the solution, and the amount of product so that can be seen clearly with the naked eye, Part of this salt precipitates after less than a half hour and the other part keeps suspended in the solution, and it was noted that (5ml) of each of the reagent solution or metal ion solution, which has the least volume in the mixture, leads to the formation of ($H^+ + Cl^-$) in the solution (or when the two volumes is equal), which delays access to the end of the first equivalence point by (2.5ml) of alkali solution, this observation is applied on all studied mixtures.

Also it is noted long transition region between the equivalence points, it may due to the presence of an excess of non-linked reagent with metal ion. In addition, reagent molecules ionize partially (first hydroxyl group) and consume larger volume of the alkali solution to get to the second equivalence point, and that is leading to less consumption amount of alkali solution to get the first equivalence point due to the formation of buffer when adding the (NaOH) solution.

[***pH4,*** (10ml $CuCl_2$+15ml ARS) solution] curve shows approaching the two equivalence points of each other by increasing the volume of the metal ion solution and decreasing the surplus of the reagent volume.

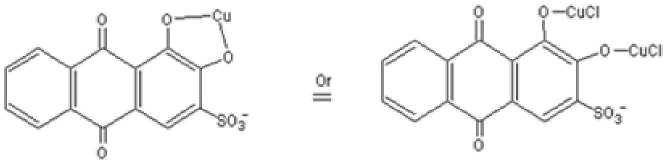
Comparing the (***pH4***) and [***pH5***, (12.5ml $CuCl_2$+12.5ml ARS) solution] curves, we find that the volumes of each solution into the mixture of the (***pH5***) curve are the appropriate volumes to form the best reaction stoichiometry (**1:1**), also should be noted that the result formula remains as a salt formula until access to the appropriate acidity to form a complex at the first equivalence point, where the complex is expected to form in accordance with the following reaction:



--------(2)

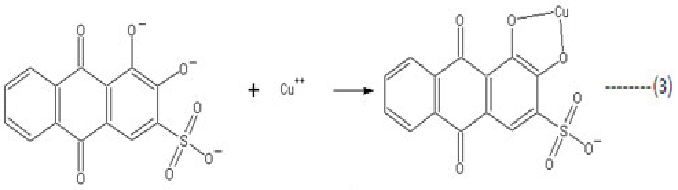
Turning to the study of (***pH6***) curve, it shows the increasing in the length of the transition region between the two equivalence points by comparing with the (***pH5***) curve, and this evidence of an excess of metal ions by comparing with the (***pH1***) curve, and this confirm that the reaction stoichiometry is (**1:1**).

When [***pH7***, (20ml $CuCl_2$+5ml ARS) solution] curve shows the increase in the length of the transition region between the two equivalence points, that it indicate to the metal ions excess. Finally, it should be signed to the reaction between the metal ions and the reagent ions at the equivalence point of the second (-OH) group which points to the reagent displacement completely, where there are two possibilities for product formula. So it is either the formed pentagonal ring or two linked ($CuCl^+$) ions with a reagent ion according to the following formulas:



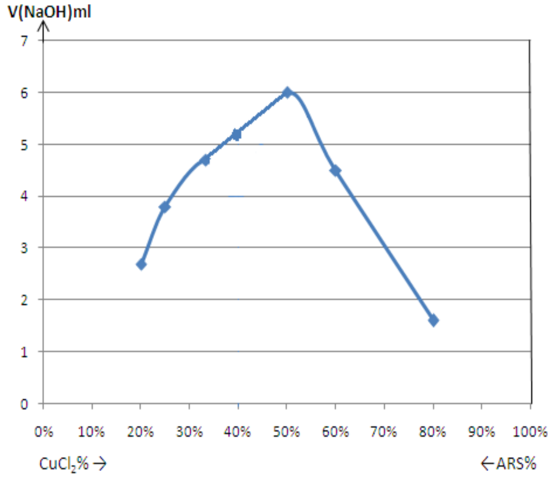
Scheme (2): Two possibilities for product formula.

The previous **scheme(2)** shows that it is expected that the first formula, which is on the left, be the likely impact of the reaction product depending on the displacement reaction (B); that means, the ($CuCl^+$) does not exist in this case. It also shows the titration of the second (-OH) group and surplus ($CuCl_2$) together because of accessing to alkali medium. In conclude, the expected reaction in alkaline media is:



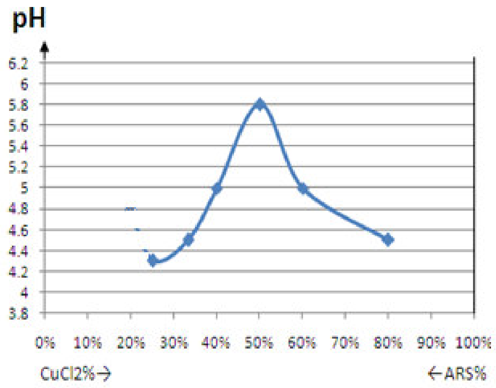
*- ***(Mixtures pH values and the consumed volume of the alkali solution) denotes at the end of the first titration point:***

The first equivalence point of the various mixtures was focused on, because each of them provides the fitting medium (suitable pH value) to form a complex as we noted previously. By considering the titration curves for the remaining percentages which are evident in [***pH8***, (8.3333ml $CuCl_2$+16.6666ml ARS) solution] and [***pH9***, (6.25ml $CuCl_2$+18.75ml ARS) solution] curves in **Figure(1)** and drawing the curve of the consumed alkali-solution volume at the first equivalence point for all ratios, the following figure has been gotten:



Figure(2): the consumed volumes of (0.01M NaOH) to reach the first end points of the titration for the all various mixtures.

The previous curve shows that to get to the first equivalence point of the mix (**1:1**) consumes the largest volume of alkali solution compared to other mixtures, due to the ionizing of the most increasable protons, which are needed the most increasable volume of alkali solution for the naturalization, and this is another proof that this percentage is the correct reaction stoichiometry. As well as the fact that this curve determines the optimal pH value to form the complex. The following curve has been obtained when the pH values was taken versus the changing of the mixture composition at the first equivalence point of the titration:



Figure(3): pH values at the points of the first titration end for all various mixtures, where (0.01M NaOH) solution was used.

The previous curve shows that the value of the pH is as high as possible at reaction stoichiometry (**1:1**), where this curve shows the highest value of pH which the complex can be formed, and as a result the range of pH values was determined toward larger values that the complex structure can keep fixed without having any change, it is also noted that the highest value of pH, which complex structure remains fixed at it, is very useful in coating process. Where it is known that the higher the acidity of the medium close to the neutral medium, the better coating process [xii]. The use of this value is evidence of a small number of protons, which provide the reaction stoichiometry (**1:1**), resulting in less impact on the activity of the buffer solution, which is used to adjust the pH value if mixture solution was titrated to get to the first equivalence point of titration then the buffer solution was added. To keep the complex structure remains stable, it is preferred to work at pH value which is equal to (5). In conclude, the rang of appropriate pH values was determined to form the complex, which is (4.2 → 5.8).

*- ***Study of the concentrations effect on pH and the form of the compound:***

pH values of the various mixtures was measured without adding the buffer. The reaction stoichiometry which was indicated in **Figure(4)** to form a salt and not to form complex, that reaction stoichiometry is (**1:1**) because there is the highest proportion of salt at the end of the following curve, where each of (ARS + $CuCl_2$) compounds shares giving the acidic character of the entire solution.

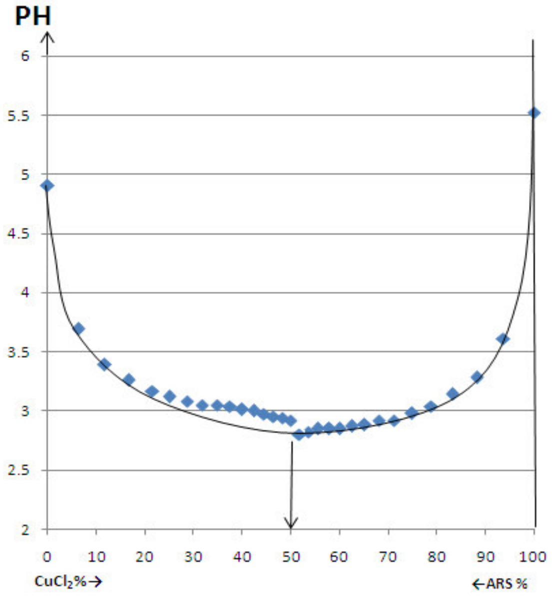
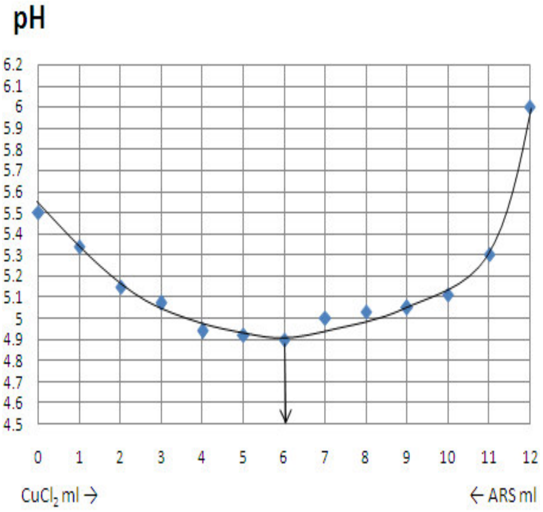


Figure (4): Curve of pH values versus mixtures compositions without adding the buffer solution.

Based on the above, when we did not use any buffer solution which has suitable range of pH values to form the complex, the mixing of reagent and metal ions solutions by (**1:1**) gives the lowest value of the pH and it is (pH=2.75) which is evident in **Figure(4)**. As a result, the accessing to lower pH value is not evidence of the forming the complex. But if concentrations were decreased for each of the two solutions to be within the range (2.5×10^{-6}-3×10^{-5}M), the pH value remains within the range (4.84-5.5) without adding the buffer solution for all studied various mixtures in this research. So two series of reagent and metal ions solutions were prepared, which has initial concentration (5.9×10^{-5}M) for each, where the total volume of each sample of the two series was equal to (12ml) with the gradient in the volume from (0.0ml) to (12ml) and complete the volume with double distilled water. Then mix all the samples of the first series with the against of the second series and adversely to apply the continuous various method, the following pH curve versus mixtures compositions was obtained:

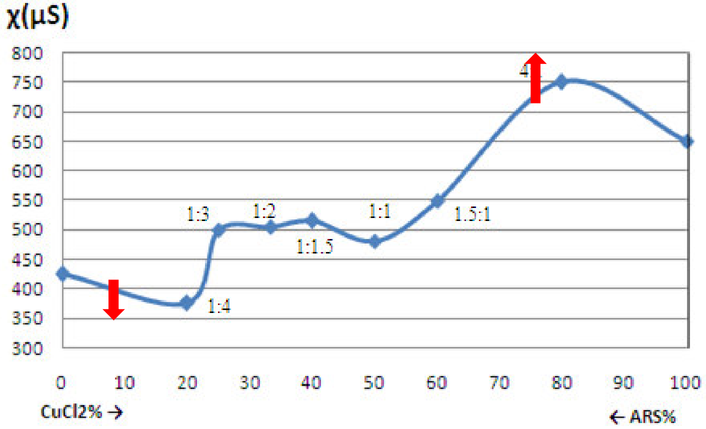


Figure(5): Curve of pH values versus mixtures compositions, where the suitable concentrations was used to remain the pH values within suitable domain, which is required for forming the complex and to calculate the reaction stoichiometry.

The previous curve indicates that the correct reaction stoichiometry is (**1:1**), because the lowest pH value indicates to the largest amount of protons which result from the linking of the largest possible amount of ($CuCl^+$) with the largest possible amount of reagent.

2 - Conductivity measurement method:

Titrated-samples curves have been obtained by measuring the conductivity of solutions. It was found that the curves of the titrated various solutions by measuring the conductivity were identical to the curves of the pH-metery method, with consideration that the titration method of measuring the conductivity is more accurate than the pH-metery method and that difference does not exceed (1ml), and **Figure(2)** remains true also for the method of conductivity measurement. So, Figure(6) was obtained from measuring the conductivity of different mixtures composition at the first equivalence point:

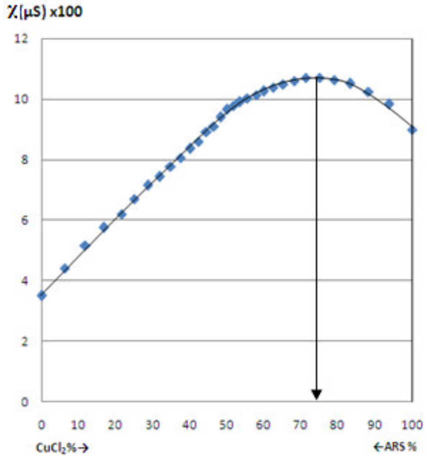


Figure(6): conductivity values of the different mixtures compositions at the first equivalence point of titration.

Figure(6) shows the best studied mixtures, because (1:4) and (4:1) mixtures have very high or very low conductivity values respectively indicating to a excess quantity of one of reagents in mixtures solutions, while the best mixtures are (1:3), (1:2) and (1:1), in addition to the ratios between them.

Study of the concentration effect on the conductivity values of the mixtures solutions:

The following **figure(7)** shows that the increasing of the copper ions concentration causes the increasing of the conductivity of the overall solution even reach the percentage (75%), after that the conductivity starts decline, it may be due to the precipitation of salt when the used concentrations are (4×10^{-3}M), which leads to obstruction of electrolyte movement in the solution, The comparison between **figure(4)** and **figure(7)** emphasizes that the complex is not exist, which results in protons to get the highest value of conductivity and the lowest value of the pH at that reaction stoichiometry which is the largest between reagent and metal ions, because the pH range never helps to form the complex. Where the reaction stoichiometry that has been reached in **figure(7)** is (**3:1**), while the reaction stoichiometry in the pH-metry method was (**1:1**) and this contradiction is further evidence of the lack of any form of the complex in each case of the previous cases.



Figure(7): Curve of the conductivity values versus the various mixtures compositions.

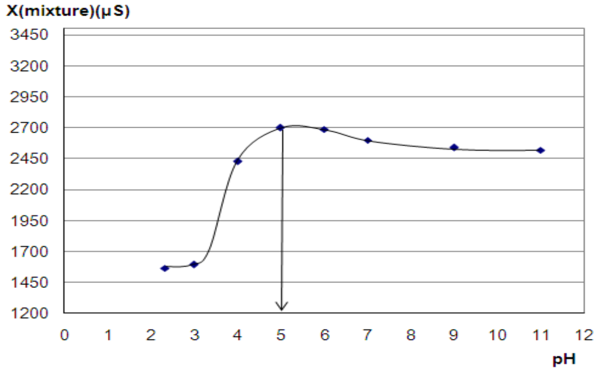
****- Study of the pH values effect on the conductivity of the mixtures:***

The appropriate conditions have been determined to form the complex, where the conductivity method and buffer solution were used to control the pH value, the following table shows the used mixture composition versus the pH values and conductivity values of the mixture:

	pH	χ(mixture)(μS)
(ARS)(9ml)+(CuCl$_2$)(3ml)	2.33	1568
	3	1594
	4	2430
	5	2700
	6	2690
	7	2600
	9	2540
	11	2520
	(CH3COOH+NaOH)(22.5ml)	

Table (1): Statement of used mixture composition and conductivity values at the different pH values.

Then the relationship between the pH values and the conductivity values was drawn as the following:



Figure(8): The curve of the conductivity values versus the various pH values to determine the suitable value of pH.

It was found that appropriate pH value to get the highest value of the conductivity of the solution is equal to (pH=5), where this value refers to the conductivity value to form the complex in specified optimal conditions, which means the existence of the highest amount of protons in these conditions.

Using of conductivity method to determine the reaction stoichiometry:

the reaction stoichiometry has been studied by taking (12ml) of metal ions solution and adding (12ml) of the buffer solution to adjust the pH value which is (pH=5), then adding (24ml) of reagent solution in batches where each batch was (1ml) and measuring the conductivity. Conductivity values were corrected by the following formula [xiii]:

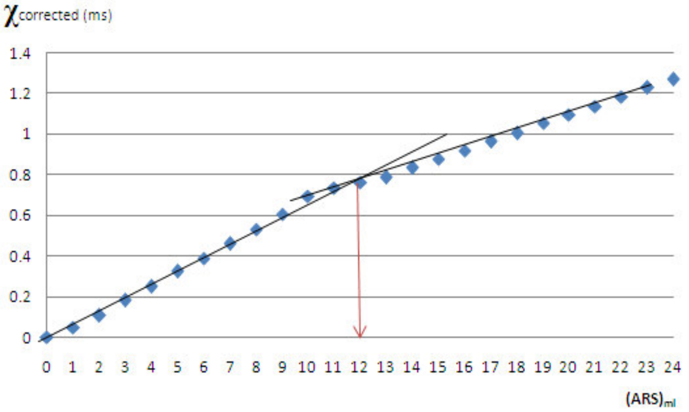
{[vml(ARS) + Vml($CuCl_2$)]/Vml($CuCl_2$)} × observed conductivity (mS) = corrected conductivity (mS)

The results were put in the following table:

$V_{ml}(CuCl_2)$	$v_{ml}(ARS)$	observed conductivity (mS)	corrected conductivity (mS)
12	**0**	**0**	**0**
12	**1**	**0.046**	**0.04792**
12	**2**	**0.098**	**0.1062**
12	**3**	**0.16**	**0.18**
12	**4**	**0.214**	**0.2497**
12	**5**	**0.268**	**0.32383**
12	**6**	**0.31**	**0.3875**
12	**7**	**0.356**	**0.45983**
12	**8**	**0.397**	**0.52933**
12	**9**	**0.44**	**0.605**
12	**10**	**0.49**	**0.6942**
12	**11**	**0.505**	**0.7365**
12	**12**	**0.508**	**0.762**
12	**13**	**0.51**	**0.7863**
12	**14**	**0.526**	**0.83283**
12	**15**	**0.539**	**0.8759**
12	**16**	**0.55**	**0.9167**
12	**17**	**0.563**	**0.9618**
12	**18**	**0.573**	**1.0028**
12	**19**	**0.587**	**1.05171**
12	**20**	**0.598**	**1.09633**
12	**21**	**0.605**	**1.1344**
12	**22**	**0.617**	**1.1826**
12	**23**	**0.627**	**1.2279**
12	**24**	**0.634**	**1.268**

Table(2): Statement of used mixture composition and conductivity values at the different pH values.

The relationship between the corrected conductivity values and the additive volumes of the reagent solution was drawn as in the following:

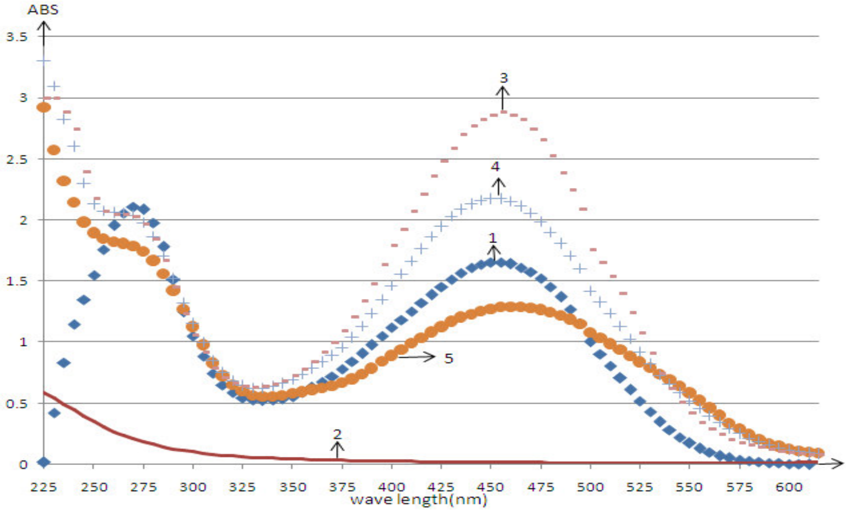


Figure(9): Statement of the reaction stoichiometry by using the conductivity method, (12ml) of metal ions solution with (12ml) of buffer solution and adding (24ml) of reagent solution gradually.

The previous **figure(9)** confirms the link proportion between the metal ions (Cu^{2+}) and reagent ions (ARS^-) which is equal to (**1:1**).

3 - Spectrophotometric method:

Several experiments were done in order to access to the characteristic spectrum of the complex and without use any buffer solution or change in pH value:

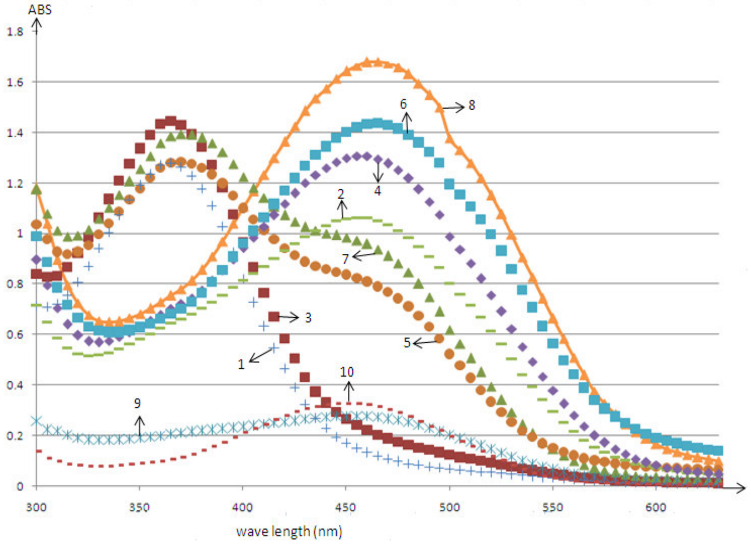


Figure(10): Absorption spectrum change with change of ratio which is between the volume of the reagent solution and the volume of the metal ions solution: 1- spectrum of (0.004M ARS) solution, 2- spectrum of (0.004M $CuCl_2$) solution, 3- spectrum of (12ml ARS+8ml $CuCl_2$) mixture solution, 4- spectrum of (10ml ARS+10ml $CuCl_2$) mixture solution, 5- spectrum of (8ml ARS+12ml $CuCl_2$) mixture solution.

The previous **figure(10)** shows that there is no formed-complex spectrum in the solution distinct from the reagent spectrum, and there is no any shift of reagent spectrum when its solution mixes with metal ions solution with a variable concentrations. That state happens when there is no any suitable adjustment of the pH value which is required to form the complex.

The effect of pH values on the absorption spectrum of the studied solution:

the appropriate pH value was determined by realizing the experiments within part of the activity range of the buffer solution, the following figure shows how to obtain a characteristic spectrum of the complex and shows that the best value of the pH values is (pH=5):

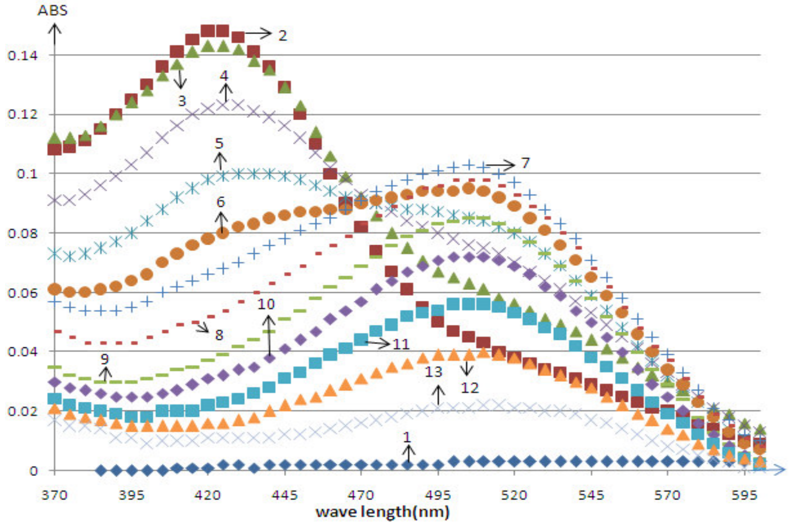


Figure(11): Change of absorption spectrum of the reagent solution by adding the metal ions solution, where the concentration is (9.6×10^{-4}M) for both of them at Selected pH values:

1-spectrum of (ARS) (pH = 4), 2- spectrum of (ARS+$CuCl_2$) (pH=4), 3- spectrum of (ARS) (pH=4.5), 4-spectrum of (ARS+$CuCl_2$) (pH=4.5), 5-spectrum of (ARS) (pH=5), 6-spectrum of (ARS+$CuCl_2$) (pH=5), 7-spectrum of (ARS) (pH=5.5), 8- spectrum of (ARS + $CuCl_2$) (pH=5.5), 9- spectrum of (ARS) (pH=6), 10-spectrum of (ARS+$CuCl_2$) (pH=10).

Determining the required reaction stoichiometry to form the complex:

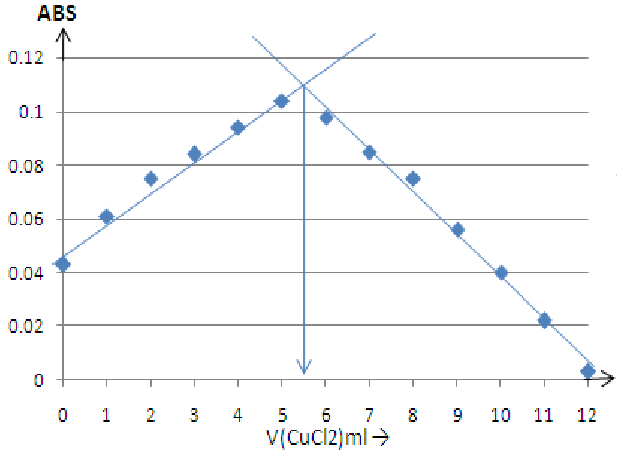
To determine the reaction stoichiometry, and changing the concentration of reagent solution and metal ions solution. The preparation of a standard series of solutions was done, where the volume of buffer solution in each sample was equal to (12ml) and Stoke solution of both (metal ions solution and reagent solution) was equal to (5.9×10^{-5}M), then we measured the absorbance change at variable wavelength versus double distilled water. The following figure shows the reaction stoichiometry:



Figure(12): 1- spectrum of (12ml $CuCl_2$), 2- spectrum (12ml ARS), 3- spectrum of (1ml $CuCl_2$+11ml ARS), 4- spectrum of (2ml $CuCl_2$+10ml ARS), 5- spectrum of (3ml $CuCl_2$+9ml ARS), 6- spectrum of (4ml $CuCl_2$+8ml ARS), 7- spectrum of (5ml $CuCl_2$+7ml ARS), 8- spectrum of (6ml $CuCl_2$+6ml ARS), 9- spectrum of (7ml $CuCl_2$+5ml ARS), 10-spectrum of (8ml $CuCl_2$+4ml ARS), 11- spectrum of (9ml $CuCl_2$+3ml ARS), 12- spectrum (10ml $CuCl_2$+2ml ARS), 13- spectrum of (11ml $CuCl_2$+1ml ARS).

Depending on the Job's method which is continuous variety the reaction stoichiometry has been calculated when the wavelength was (510nm) as the following chart shows:

V(ARS)ml	V($CuCl_2$)ml	ABS
12	0	0.043
11	1	0.061
10	2	0.075
9	3	0.084
8	4	0.094
7	5	0.104
6	6	0.098
5	7	0.085
4	8	0.075
3	9	0.056
2	10	0.04
1	11	0.022
0	12	0.003



Figure(13): Continuous variety method to calculate the reaction stoichiometry (change of the absorbance values versus the change of the concentrations with the constancy of total volume.

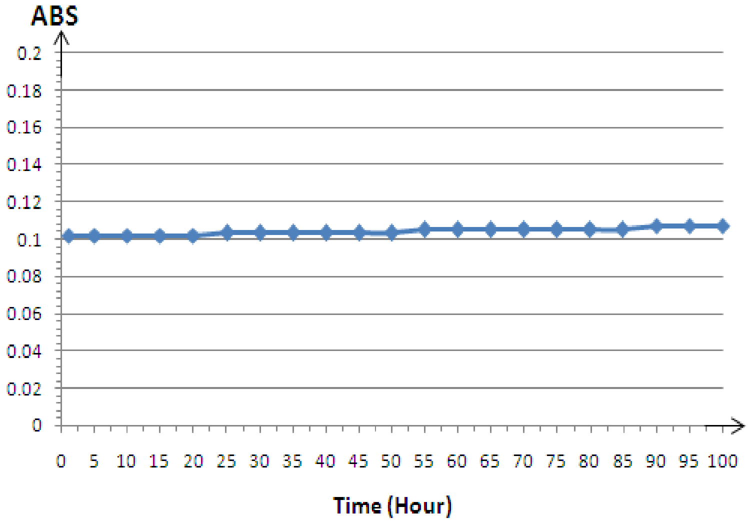
The previous **figure(13)** determines the reaction stoichiometry which is (**1:1**) by doing the following accounts:

$$\{V(M) / [V(M) + V(L)]\} = 0.46, \{V(L) / [V(M) + V(L)]\} = 0.54$$

$$\Rightarrow [V(L) / V(M)] = 1.18 \approx 1 \Rightarrow V(L) = V(M)$$

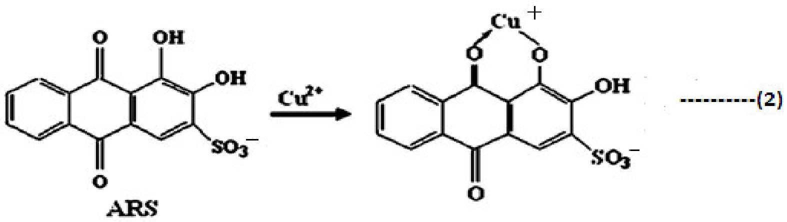
Study of the effect of changing times on the absorbency of the formed complex (study of the stability of the complex during the time):

The change of complex absorbance versus times has been studied where the wavelength was (510nm), and found that the complex is stable away from a high temperature and light. The following figure shows that:



Figure(14): Absorbance change with time, where the concentration is equal to (1.5×10^{-5}M) for each of metal ions solution and reagent solution in the same solution.

Figure(14) shows the change of absorbance of complex with the time, away from a high temperature and light. As a result, the expected reaction under those conditions and that has been reached in several ways:



4 - Electroplating of copper(II) experimentally:

The use of bath with anodic graphite paste causes a heavy sludge in the solution, in addition to causing a change in the composition of the solution resulting from the mixing of graphite particles and paraffin oil with solution components, especially if stirring of solution is used, and all of that gives unsatisfactory results unfortunately. So the other mentioned two kinds of coating bath were used, and the studies were carried out as in the following:

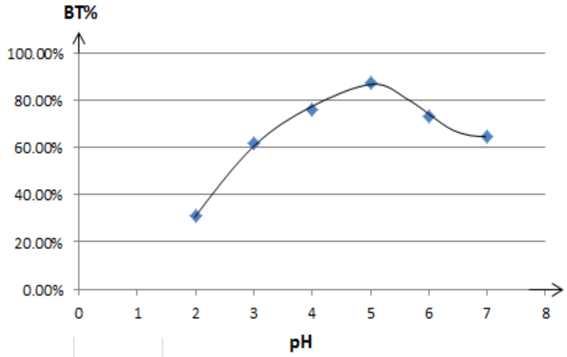
Study of current efficiency of copper coating versus pH values:

Experiments were done at (V=2-5v, i=3 mA/cm^2, t=1 h), and the results were obtained and put in the following table:

pH	Cathode weight (g) before coating	Cathode weight (g) after coating	Copper weight (g)	Current efficiency BT%
2	**46.9660**	**46.9671**	**0.0011**	**30.92%**
3	**46.4034**	**46.4056**	**0.0022**	**61.85%**
4	**46.5246**	**46.5273**	**0.0027**	**75.91%**
5	**46.8085**	**46.8116**	**0.0031**	**87.15%**
6	**46.5358**	**46.5384**	**0.0026**	**73.1%**
7	**46.6728**	**46.6751**	**0.0023**	**64.66%**

Table(3): Current efficiency values of copper coating versus pH values.

The relationship between the current efficiency values and pH values has been drawn as the following curve:



Figure(15): Curve of Current efficiency values of copper coating versus pH values.

Figure(15) shows that the best current efficiency value is at (pH=5).

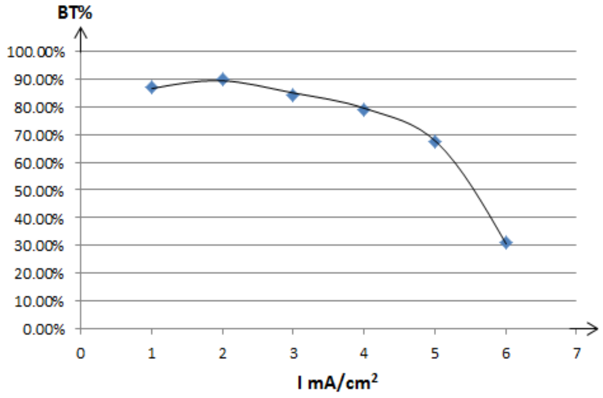
Study of current efficiency of copper coating versus current density (i mA/cm^2):

Experiments were done at (V=2-5v, pH=5, t=1 h), and the results were obtained and put in the following table:

i mA/cm^2)(	Cathode weight (g) before coating	Cathode weight (g) after coating	Copper weight (g)	Current efficiency BT%
1	**46.6563**	**46.6573**	**0.0010**	**87.15%**
2	**46.8797**	**46.8818**	**0.0021**	**89.96%**
3	**46.6873**	**46.6903**	**0.0030**	**84.34%**
4	**46.9829**	**46.9866**	**0.0037**	**78.72%**
5	**46.4913**	**46.4953**	**0.0040**	**67.47%**
6	**46.3730**	**46.3752**	**0.0022**	**30.92%**

Table(4): Current efficiency values of copper coating versus current density values.

The relationship between current efficiency values and current density values has been drawn as the following curve:



Figure(16): Curve of Current efficiency values of copper coating versus current density values.

Figure(16) shows that the best current efficiency value is at (i=1.5-2 mA/cm^2).

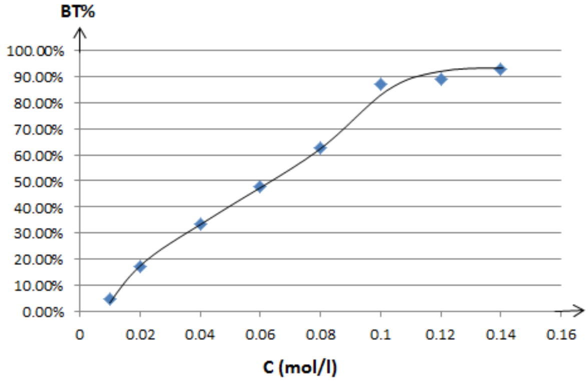
Study of current efficiency of copper coating versus molarity concentration (C mole/l):

Experiments were done at (V=2-5v, pH=5, t=1 h, i=2 mA/cm^2), and the results were obtained and put in the following table:

C (mol/l)	Cathode weight (g) before coating	Cathode weight (g) after coating	Copper weight (g)	Current efficiency BT%
0.01	**46.7599**	**46.7600**	**0.0001**	**4.718%**
0.02	**46.9600**	**46.0100**	**0.0004**	**17.435%**
0.04	**46.5492**	**46.5500**	**0.0008**	**33.452%**
0.06	**46.1089**	**46.1100**	**0.0012**	**47.985%**
0.08	**46.4907**	**46.4922**	**0.0015**	**62.657%**
0.1	**46.1587**	**46.1607**	**0.0020**	**86.782%**
0.12	**46.7848**	**46.7869**	**0.0021**	**88.875%**
0.14	**46.3177**	**46.3199**	**0.0022**	**92.79%**

Table(4): Current efficiency values of copper coating versus molarity concentration values.

The relationship between current efficiency values and molarity concentration values has been drawn as the following curve:

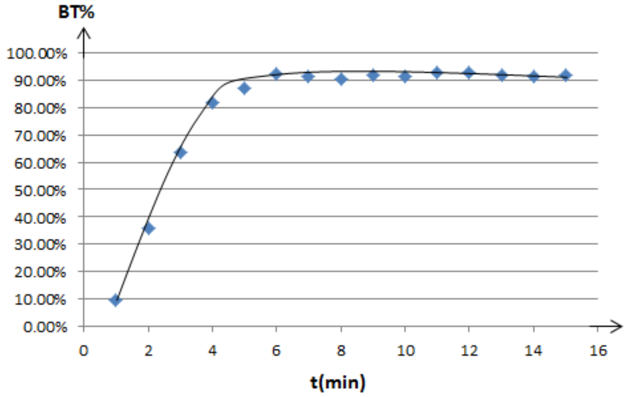


Figure(17): Curve of Current efficiency values of copper coating versus molarity concentration values.

Figure(17) shows that the best current efficiency value is at (C=0.1 M).

Study of current efficiency of copper coating versus the time (t min):

Experiments were done at (V=2-5 V, pH=5, i=2 mA/cm^2), and the relationship between current efficiency values and the time has been drawn as the following curve:



Figure(18): Curve of Current efficiency values of copper coating versus time values.

Figure(18) shows that the best current efficiency value is at (t=5 min).

Calculation of coating copper film thickness after applying the appropriate operational conditions:

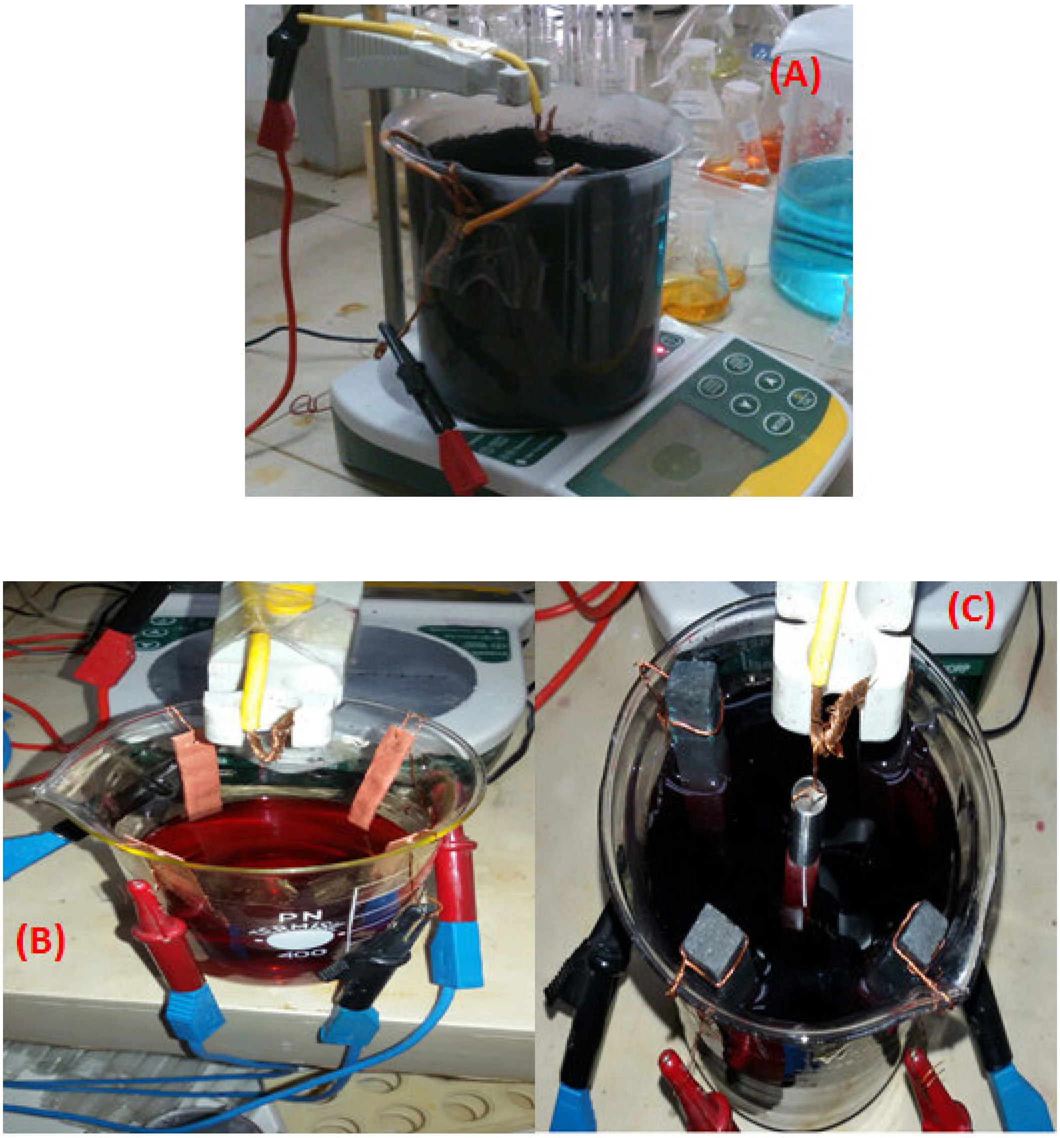
The film thickness of copper which was coated on the industrial iron (steel) at the appropriate operating conditions (V=2-5v, i=2 mA/cm^2, pH=5, t=5 min, C=0.1 M) have been calculated by using the following relationship [35]:

$$d = \frac{M_M}{\rho .\, S}$$

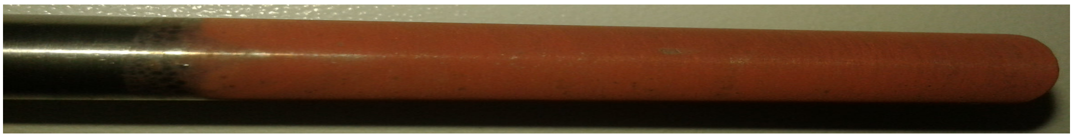
The thickness of the coating film is: d=1.756 × 10^{-5} cm =1.756 × 10^{-1} µm.

A good coating copper layer on the industrial iron (steel) is obtained either using the insoluble dry graphite anodes or using the anodes of soluble sheets of copper, and the following conditions is the suitable operating conditions:

(V=2-5 V, i=2 mA/cm^2, pH=5, t=5 min, C=0.1 M) $\Longrightarrow$ d = 1.756 × 10^{-1} µm

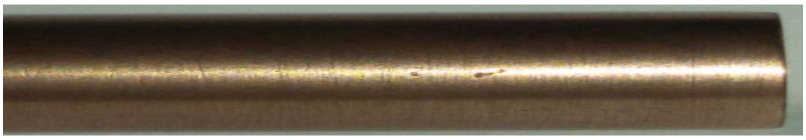


Figure(19): Three kinds of coating bath, (A): coating bath with anodic graphite paste, (B): coating bath with anodic soluble copper, (C): coating bath with anodic insoluble graphite.



Figure(20): Electrode of industrial iron coated with copper in a bad operating conditions.

Figure(21): Electrode of industrial iron coated with copper in the appropriate operating conditions.



Figure(21a): Electrode of industrial iron coated with copper in the appropriate operating conditions (close section).

Conclusion

1- There is no any complex formation complex by mixing the reactants, which have (0.004M) concentration, without the adjustment of pH value, but the complex forms when the concentrations are reduced to become (10^{-5}M) or when the pH value is adjusted to be equal to (pH=5).
2- The complex forms at suitable pH value for coating process because it is near to the neutral medium.
3- The reaction stoichiometry of formed complex (ARS – Cu II) is (**1:1**).
4- The use of bath with anodic graphite paste causes a heavy sludge in the solution, in addition to causing a change in the composition of the solution resulting from the mixing of graphite particles and paraffin oil with solution components, especially if stirring of solution is used, and all of that gives unsatisfactory results.
5- A good coating copper layer on the industrial iron (steel) is obtained either using the insoluble dry graphite anodes or using the anodes of soluble sheets of copper, and the following conditions is the suitable operating conditions:

$$(V=2\text{-}5\ V,\ i=2\ mA/cm^2,\ pH=5,\ t=5\ min,\ C=0.1\ M) \Longrightarrow d = 1.756 \times 10^{-1}\ \mu m$$

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