

## **ELECTROLYTIC PRODUCTION OF POTASSIUM BROMATE USING GRAPHITE SUBSTRATE LEAD DIOXIDE (GSLD) ANODE**

**AHMED DAHAM WIHEEB**

**Chem. Eng. Dept., College of Eng., Tikrit University**

### **ABSTRACT**

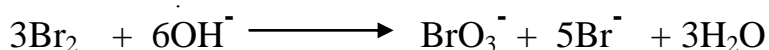
Graphite substrate lead dioxide (GSLD) was used to make a suitable anode for the production of potassium bromate from potassium bromide. This anode has been used successfully in the presence of certain addition agents (like potassium dichromate) as a replacement for graphite anode. A laboratory electrolytic cell was designed to produce of potassium bromate. A solution of potassium bromide (240 g/l) and potassium bromate (20 g/l) is electrolyzed in batch wise. The effect of anodic current density, temperature, and starting PH of electrolyte on the current efficiency of bromate formation was studied. High current efficiency of about 92 – 94 % was obtained by using (GSLD).

### **KEY WORDS**

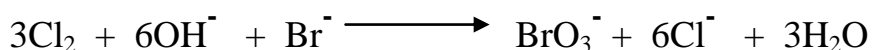
Potassium bromate, Lead dioxide anode, Potassium bromide oxidation , Electrolytic cell

## INTRODUCTION

Bromates used as valuable oxidizing agents and brominating agents in analytical chemistry <sup>[1]</sup> and in beauty shop exclusively for cold permanent waves. Potassium bromate is used to smaller extent as an additive for foodstuff ( such as improving the quality of flour ) as well as for woolen textile finishing , while the sodium bromate is effective as an additive for the finishing of metal surfaces by phosphoric acid <sup>[2]</sup>. Bromates can be formed by the disproportionation of bromine in basic solution:



Boiling the solution speeds the conversion of intermediate hypobromites and bromites to bromate. The less soluble bromate can be separated from the halide by fractional crystallization <sup>[3]</sup>. Also bromates can be formed by another method that is often more economical is the oxidation of bromides into bromates by hypochlorites in aqueous solution . This can be done by passing chlorine into alkaline bromide solution <sup>[4]</sup>.



Another method to produced alkali bromates are usually prepared by electrolysis of bromide solutions, in the presence of depolarizing ion such as dichromate, and the electrolytic preparation of bromates is the most elegant method <sup>[1, 5, 6]</sup>. Usually it is prepared at graphite anode ,and the platinized titanium anode has also reported . In the present work the lead dioxide anode is

used and it is prepared by electrodepositing the oxide in a smooth and adherent form on graphite base material.

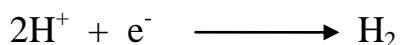
## THEORY

Bromates are prepared electrochemically by using an electrolytic cell, which consists of anode and cathode. The anodic reactions in bromate formation may be represented as follows [2]:



These reactions are similar to those witnessed in the chlorate formation except for some small differences [7]. Reaction (4) is about 100 times faster than that in chlorate formation. On the other hand, reactions (2) and (3) seem to occur imperfectly compared with the reactions in chlorate formation by comparing the hydrolysis constant of  $\text{Br}_2$  with that of  $\text{Cl}_2$  [2].

At the cathode surface, the reduction of hydrogen ions ( $\text{H}^+$ ) to hydrogen gas ( $\text{H}_2$ ) take place [8].



Electrolytic production of bromates are usually carried out at graphite anode [1, 6, 9] as in the production of chlorate. The use of graphite, however, has some unfavorable effects. Graphite becomes eroded during the electrolysis forms mud which

continuous operation difficult. The final product also turns slightly yellow and can be decolorized only with difficulty<sup>[5]</sup>.

Usually the conventional electrolysis cell using graphite anodes are specified by the following parameters<sup>[1]</sup>.

Temperature	56 – 60 ° C
PH	8
Cell feed:	
• Potassium Bromide	10 - 25 g / L
• Potassium Bromate	210 – 240 g / L
• Potassium dichromate	2 g / L
Anode current density	22.4 Amp / dm <sup>2</sup>
Cell voltage	3.4 - 4.5 Volt
Current efficiency	88 – 90 %

Platinized titanium electrodes made by Imperial Chemical Industries Ltd., England seem to be recognized as an anode material for this object<sup>[2]</sup>. In the recent years the quest for the development of indestructible anodes either as substitute costlier anodes or to increase the life of anodes in electrochemical processes has intensified. Increasing interest in the scientific development of inert and insoluble anodes provided a healthy atmosphere meriting considerable research effort both in the improvement of existing anodes and in the development of new anodes. Graphite and platinum are widely well-known anodes in electrochemical processes and, less frequently, materials like magnetite, lead, and, lead-silver or lead-antimony alloy are

employed. But the recent researches on the indestructible or inert anodes are largely centered around the development of (i) platinum or its alloy coated over titanium and (ii) coating of oxide or mixed oxides of certain metals on suitable substrates <sup>[10]</sup> .

The main requirements for an oxide anodes are: (i) the possibility of forming ions of different valences to provide a high electrical conductivity ;(ii) a high anodic potential to evolution of oxygen, (iii) absence of rectifying contacts, and (iv) chemically inert <sup>[10,11,12]</sup> .

Lead dioxide satisfies the major requirements for the oxide anodes. It has a high anodic potential for oxygen evolution and it is inert for most chemical solutions <sup>[12,13]</sup> . Therefore, it is used in an inorganic preparations like chlorate <sup>[7]</sup> , perchlorate <sup>[11,13]</sup> , bromates , iodates and , periodates .

## **EXPERIMENTAL WORK**

### **Cell Assembly**

The cell assembly consisted of a 250 ml tall-form beaker with a cell cover made of “Perspex “with holes to introduce anode, cathode, and thermocouple. The cell was placed in an outer water bath to heat the electrolyte to the desired temperature .A copper cooling coil was passed around the cell to cooling it. The liquid passing through the coil is water which is coming from cold water container by pumping it to the coil. A

contactor was connected with the pump and thermocouple to control the temperature of the cell through the experiment running. Graphite substrate Lead dioxide (GSLD) anode prepared by depositing lead dioxide on graphite rod ( 10 cm length & 1 cm diameter ) from lead nitrate bath ( 350 g/L ) , at temperature range (60 to 65 °C ) and pH range ( 4 - 4.5 ) . The lead dioxide deposited on graphite rod until the diameter of the rod become 1.2 cm. A rotating technique for cylindrical rod was used <sup>[13]</sup>. Two bent, perforated stainless steel plates (5.5 x 8.5 cm) acted as cathodes. Anode – cathode spacing was 1 cm. A glass spacer was introduced in between the anode and cathode to avoid shorting, as shown in Fig.(1).

### **Electrolyte**

The electrolyte was prepared by dissolving 240 g of potassium bromide in distilled water to give 1000 ml of solution. A small amount of potassium bromate (nearly 20 g/l) was added to the electrolyte, which it reported to be favorable for isolation of the product <sup>[14]</sup>. The initial concentration of bromide and bromate of solution was determined by the iodometric method <sup>[15]</sup>. For each experiment, 200 ml of electrolyte was used and 2 g/l of potassium dichromate was added to the electrolyte. The initial pH of the electrolyte was adjusted by adding dilute alkali (NaOH 0.1 N).

## **Electrolysis**

A selenium rectifier provided direct current and in each experiment the quantity of electricity required theoretically to produce 100 g/l of bromate is 6 faradays which passed unless otherwise stated. The current efficiency calculated on the basis of bromate formed in each experiment by determination the amount of the bromate formed at the end of experiment employing iodometry.

## **Description of the Experimental Procedure**

The electrolytic cell first filled with 200 ml of electrolyte for each experiment, and then it was placed in water bath and heated the electrolyte to the desired temperature. The anode, cathode, and thermocouple were dipped in the electrolyte through the holes in the cell cover at a desirable height. The power supply was switched on to provide a constant current. Also the pump was operated to adjust the temperature of the electrolyte. At the end of the theoretical time of electrolysis, the pH of the electrolyte was measured. A known amount of electrolyte (5 ml) was pipette out for analysis to determine the amount of bromate formed then the current efficiency is calculated.

## **RESULTS AND DISCUSSION**

The current efficiency for the production of potassium bromate process influenced by many variables such as anode

current density , temperature , and pH starting . The effect of each variable can be explained as follow:

### **Effect of Anode Current Density**

The effect of anode current density on the current efficiency was studied in the range of 10 to 40 Amp/dm<sup>2</sup>. The results are shown in Figs. (2) to (4). The anodic current density less than 10 Amp/dm<sup>2</sup> and temperature of 65<sup>0</sup>C the current efficiency reduced to less than (85%), but when the anodic current density higher than 10 Amp/dm<sup>2</sup> the current efficiency increases until it reaches to a maximum at 26 to 29 Amp/dm<sup>2</sup> then the current efficiency decreases again. The results can be interpreted that at low anode current density ( 10 Amp/dm<sup>2</sup> ) the anode potential not attained to a high value enough for the bromate formation that occurred at an appreciable rate, and the losses in current caused by oxygen evolution at anode surface so that the current efficiency is low. After that the current efficiency increases with increased anodic current density due to increase in anode potential until the current efficiency again lowered with increasing in anode current density due to the anode potential was reached to a higher value which is enough for the side reactions . Therefore , the current efficiency is reduced.

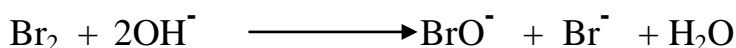
### **Effect of Temperature**

The effect of temperature on the current efficiency was studied in the range of 35 to 65 <sup>0</sup>C because the deposit lead dioxide layer disintegrates at higher temperature (> 65 <sup>0</sup>C). The



results shown in Figs. (5) to (7). It can be seen that the relation between temperature and current efficiency at different values of anodic current density and pH have the same behavior. In Fig.6 it is noticed that at temperature lower than 35<sup>0</sup>C and anodic current density of 30 Amp/dm<sup>2</sup>, the current efficiency decreases to less than (86%), while at temperature higher than 35<sup>0</sup>C the current efficiency increases to the extent that the temperature reached to the range of 55 to 60 <sup>0</sup>C, then the current efficiency decreases again.

It was demonstrated that some reactions on the anode surface are accelerated by high temperature, which has a favorable effect on current efficiency:-



The rise of current efficiency with temperature up to optimum may be due to this factor, whereas above the optimum the current efficiency decreases with increasing in temperature due to increase in the activation energy of side reactions.

### **Effect of pH starting**

The effect of pH starting of the electrolyte on current efficiency was studied in the range of 6 to 8. Figs. (8) to (11) explain the results which have the same behavior. In Fig.9 it is observed that the current efficiency is higher in pH = 8 than in pH=7 and pH=6 . The current efficiency is not much affected with the pH starting at the range of 6 to 8 because the current

efficiency varied only 2 to 3% .When the starting solution is slightly acidic and neutral or alkaline, the current efficiency was not much affected , but when the pH is maintained acidic by addition of dilute sulphuric acid, the current efficiency dropped considerably with evolution of bromide because of the bromide-bromate mixture reacting under high acidic conditions. The results showed that the current efficiency is high in slightly alkaline solution ( pH=8 ) because of the reactions on anode surface to produce bromate are occurred. High current efficiency can be attained easily by using a neutral or slightly alkaline solution of bromide at the start of the electrolysis. The effort to keep the pH in the desirable range is not necessary except the avoidance discharge of hydroxyl ions.

## CONCLUSIONS

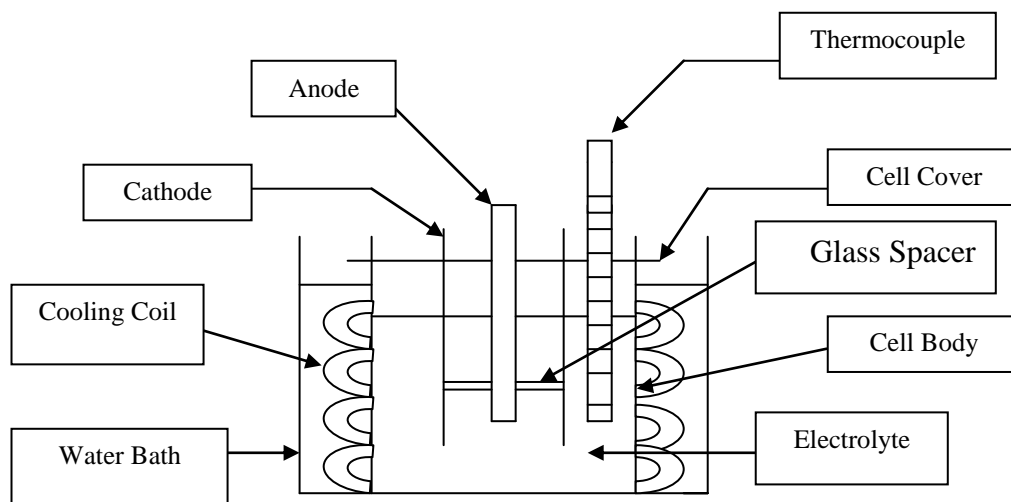
1. The (GSLD) anode is considered as the best alternative anode to graphite. It is inert and insoluble in the electrolysis process, whereas the graphite anode is eroded during the electrolysis process and forms mud, then the production need to filtration. The (GSLD) anode has a long life in the electrolysis process than graphite anode.
2. The current efficiency in the bromide oxidation process to produce bromate in a cell provided with (GSLD) anode is high (about 94%) when using anode current density in the range of 26 to 29 Amp/dm<sup>2</sup>.

3. The highest current efficiency is attained at a temperature range of 55 to 60 °C.
4. The current efficiency is not much affected with the pH starting of the electrolyte in the range of 6 to 8, but in the pH starting with pH=8 the current efficiency is higher than the pH=7 and pH=6.

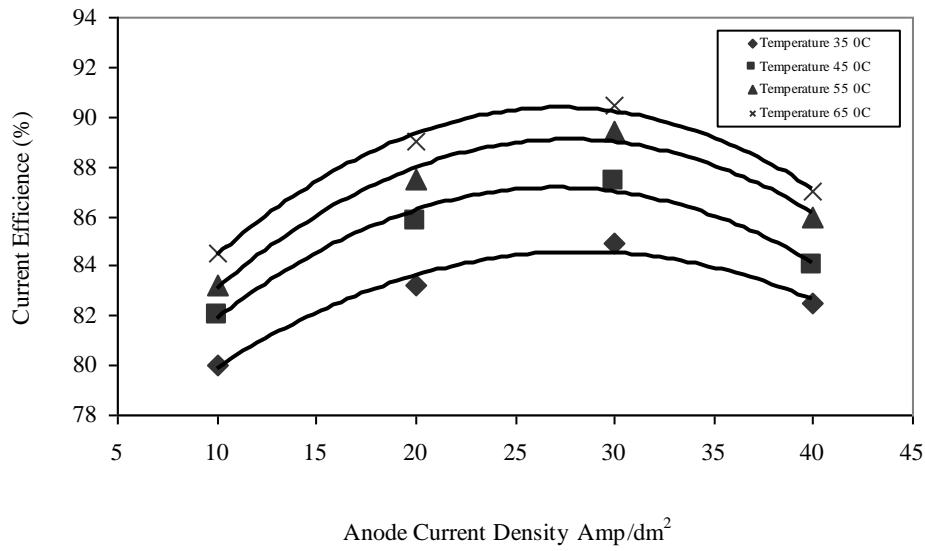
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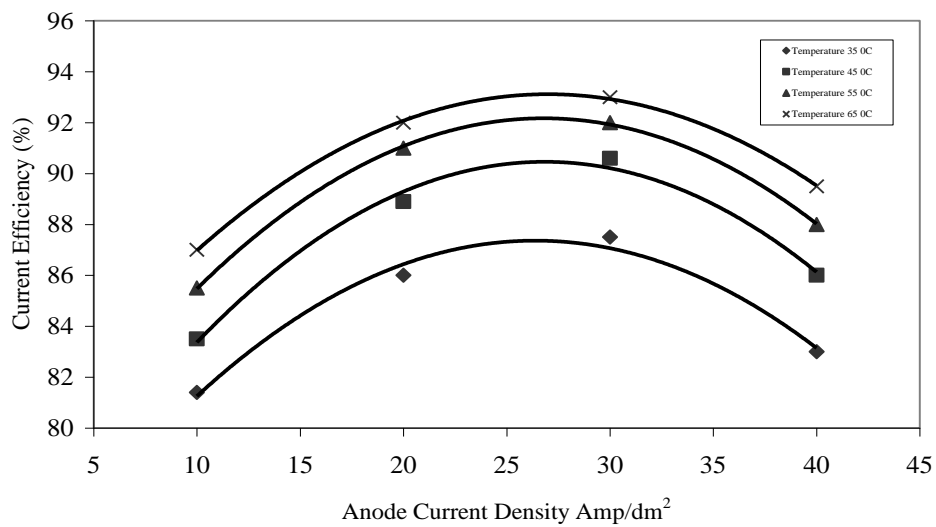
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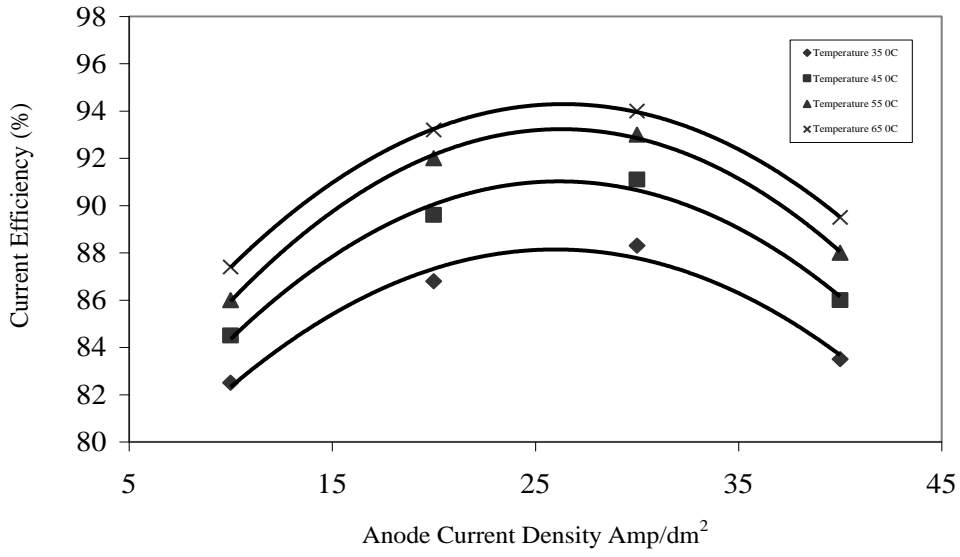
**Fig. (1) The electrochemical cell for the preparation of potassium bromate.**



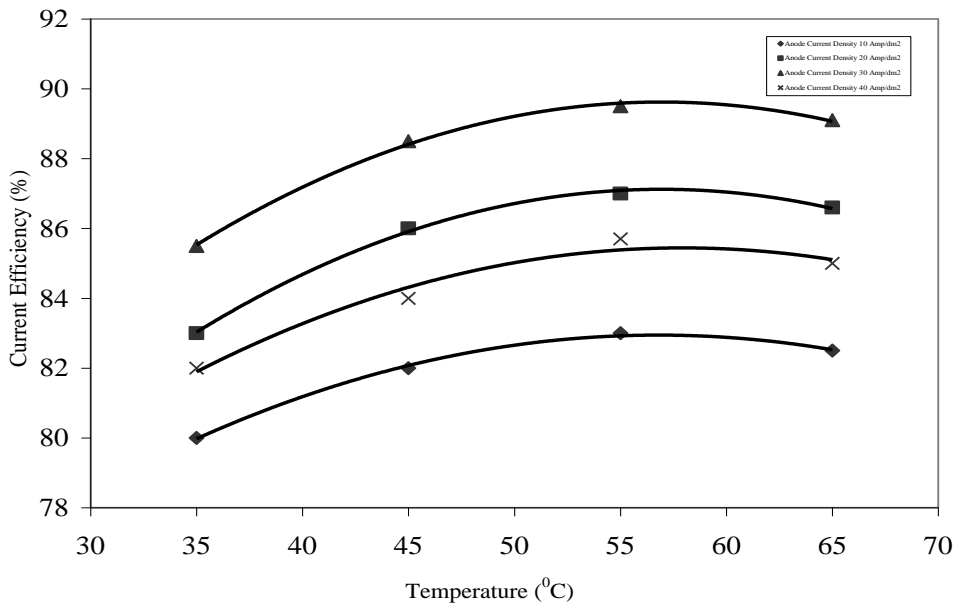
**Fig.(2) Influence of Anode Current Density on Current Efficiency at pH=6**



**Fig.(3) Influence of Anode Current Density on Current Efficiency at pH=7**



**Fig.(4) Influence of Anode Current Density on Current Efficiency at pH=8**



**Fig.(5) Influence of Temperature on Current Efficiency at pH=6**

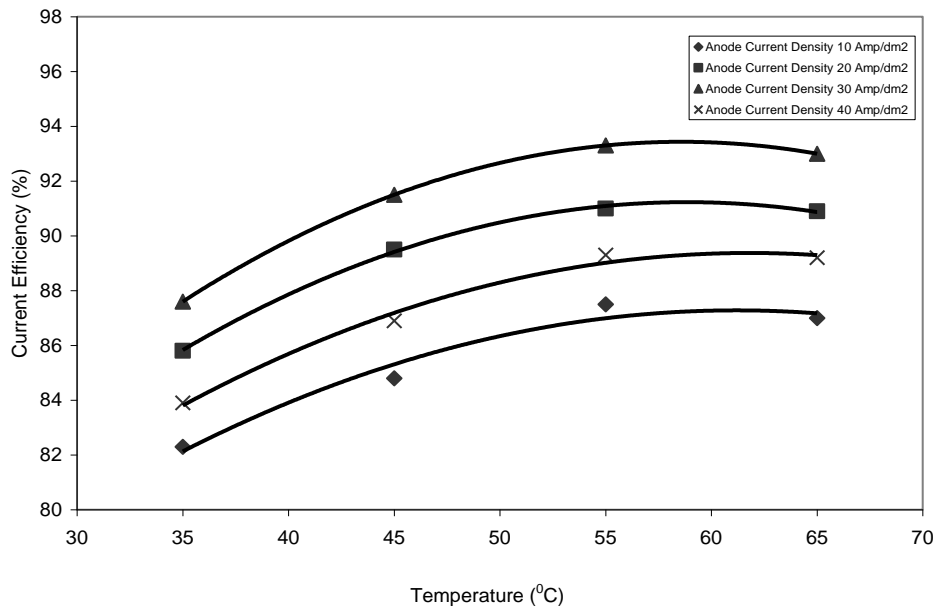


Fig.(6) Influence of Temperature on Current Efficiency at pH=7

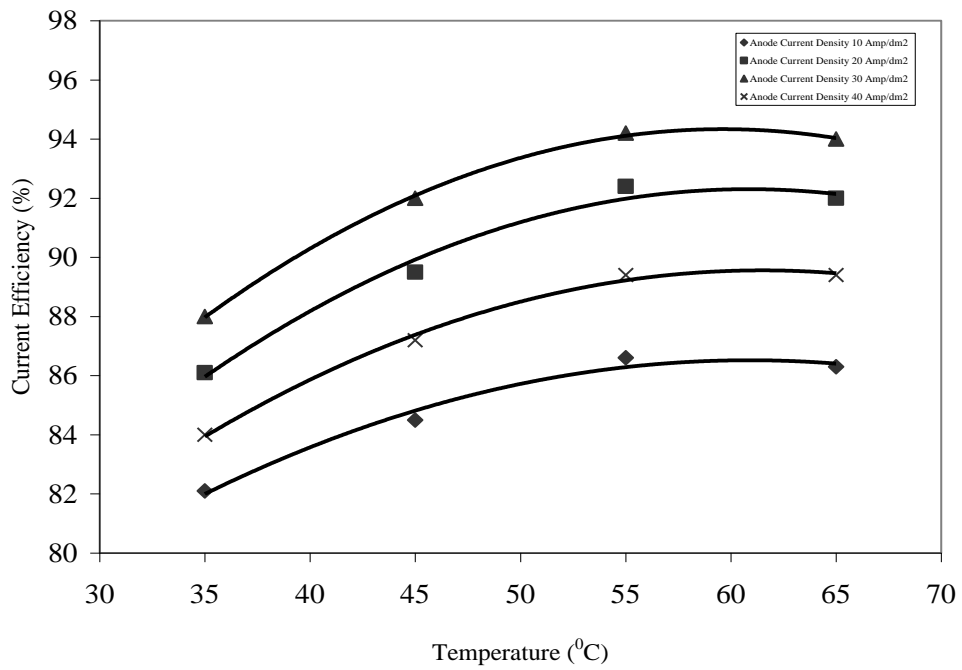
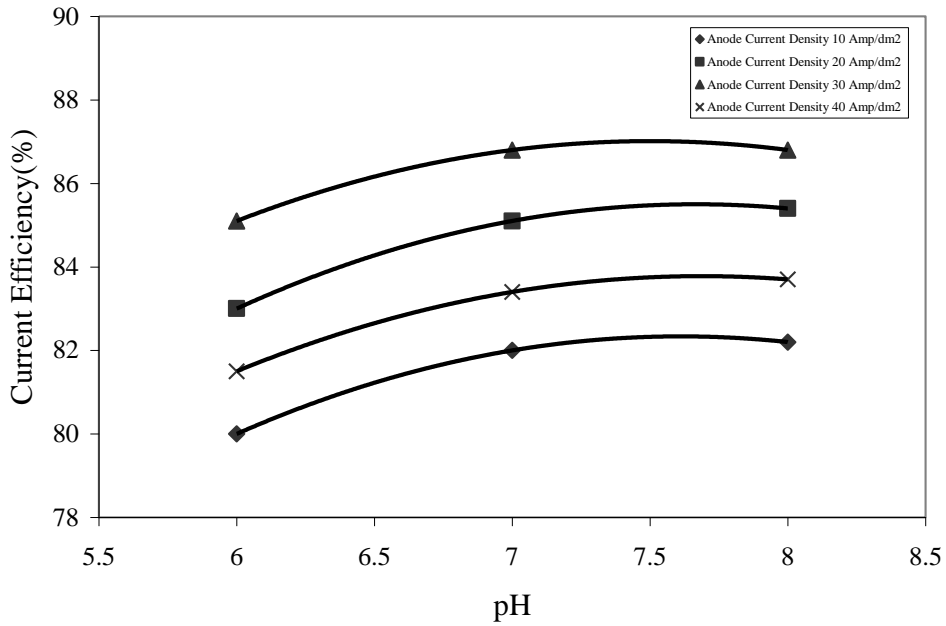
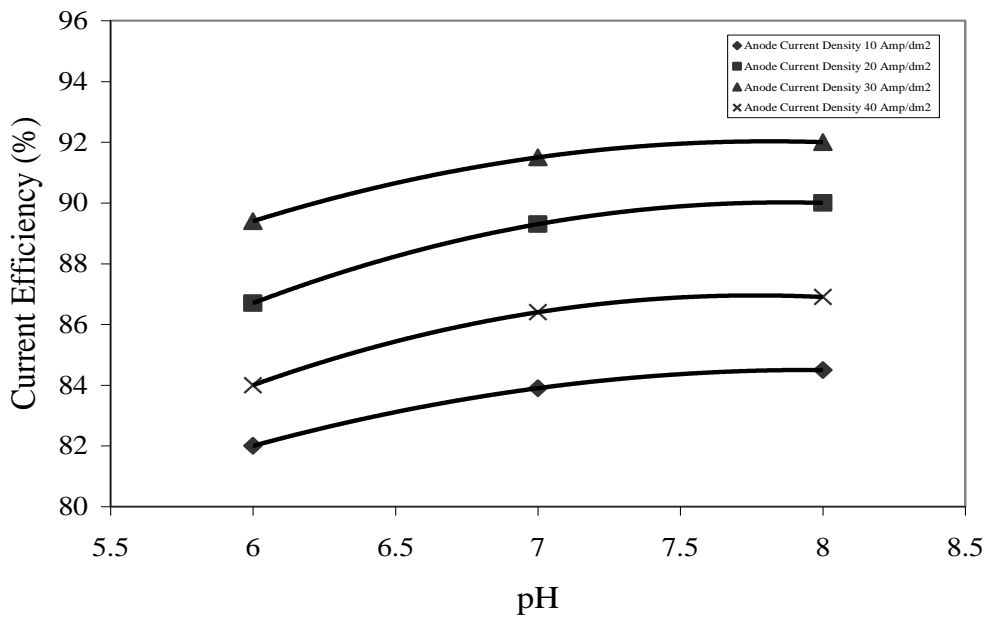


Fig.(7) Influence of Temperature on Current Efficiency at pH=8

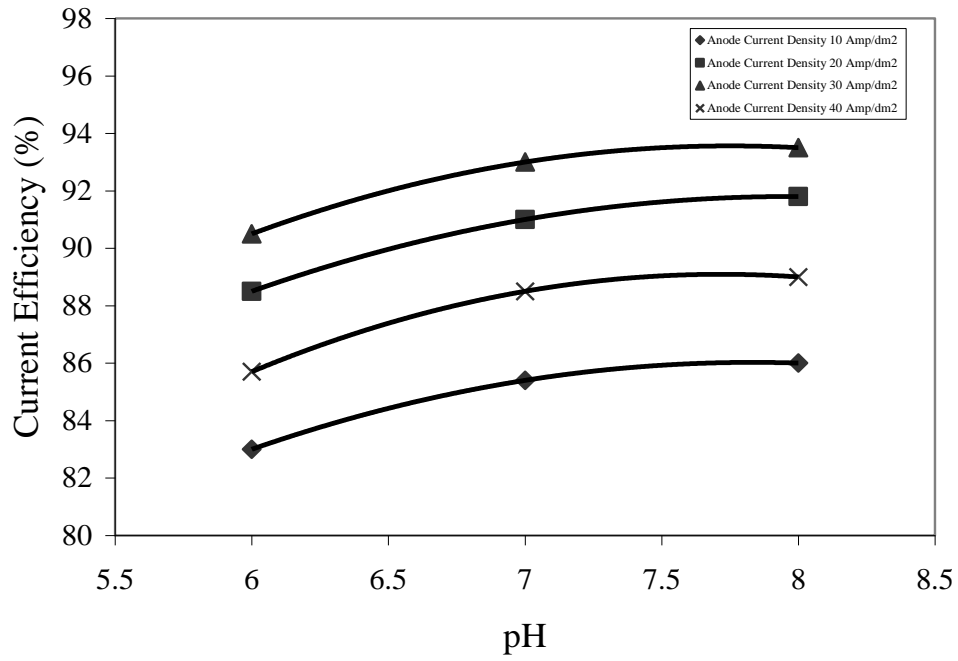




**Fig.(8) Influence of pH on Current Efficiency at Temperature 35 °C**



**Fig.(9) Influence of pH on Current Efficiency at Temperature 45 °C**



**Fig.(10) Influence of pH on Current Efficiency at Temperature 55 °C**

## الإنتاج الألكتروليتي لبرومات البوتاسيوم باستخدام الكرافيت المغطى بثاني أكسيد الرصاص (GSLD) كأنود

أحمد دحام وهيب

قسم الهندسة الكيمياوية ، كلية الهندسة ، جامعة تكريت

### الخلاصة

يستخدم الكرافيت المغطى بثاني أكسيد الرصاص (GSLD) كأنود لإنتاج برومات البوتاسيوم من بروميد البوتاسيوم بنجاح عند توفر العوامل المضافة (مثل دايكرومات البوتاسيوم) كبديل لأنود الكرافيت. وقد تم تصميم خلية الكتروليتية لأجراء التجارب والتي تتضمن التحليل الكهربائي لمحلول من بروميد البوتاسيوم بتركيز (240 غم / لتر) وبرومات البوتاسيوم بتركيز (20 غم / لتر) بالطريقة الدفعية ودراسة تأثير كثافة تيار الأنود ودرجة الحرارة ودرجة الحموضة البدائية للمحلول على كفاءة التيار لتكوين البرومات . أعلى كفاءة تيار تم الحصول عليها بحدود 92 – 94 % باستخدام (GSLD) كأنود.

### الكلمات الدالة

برومات البوتاسيوم ، ثنائي اوكسيد الرصاص كأنود ، أكسدة بروميد البوتاسيوم ، خلية الكتروليتية