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OBTAINING PYRAZINE-2,3-DICARBOXYLIC ACID THROUGH ELECTROCHEMICAL OXIDATION OF QUINOXALINE ON NICKEL ELECTRODE

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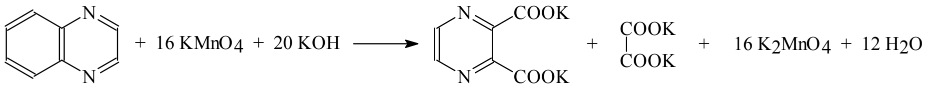
ABSTRACT. The purpose of this paper is to investigate the pyrazine-2,3-dicarboxylic acid (PDCA) synthesis process by quinoxaline chemical oxidation on nickel electrode with electrochemically regenerated potassium permanganate ($KMnO_4$). The investigation of electrode reaction was carried out through cyclic voltammetry and an efficient electrolyser for PDCA synthesis was used. Anodic regeneration of Mn^{7+} on the nickel electrode is possible. This process is favoured by KOH, Mn^{7+} (Mn^{6+} implicitly) and quinoxaline concentrations as well as by temperature increase. Current and substance efficiencies of 80% and 85%, respectively, were achieved.

Keywords: *quinoxaline, pyrazine-2,3-dicarboxylic acid, potassium permanganate, cyclic voltammetry, electrolysis, nickel electrode.*

INTRODUCTION

Medical statistics show that tuberculosis is once again on the verge of becoming a threat. This is why any method for synthesizing drugs known to have antituberculosis effects must be carefully evaluated and investigated [1].

In this context pyrazine synthesis in the most advantageous conditions is of the outmost importance. The raw stock for the production of pyrazinamide is dipotassium-pyrazine-2,3-dicarboxylic acid (K_2PDCA), which can be synthesized through chemical oxidation of quinoxaline (Q) [2-4] with potassium permanganate in alkaline medium [5-7]:



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The chemical oxidation involves a very high consumption of potassium permanganate, Q: $KMnO_4$ = 1:16M (kg/kg) [8, 9]. By contrast, the original electrochemical process for PDCA synthesis proposed by us ensures considerable higher efficiencies. This paper focuses on how these efficiencies can be obtained using the perforated nickel plate electrode.

The chemical reaction taking place in the electrochemical process is similar to that of the classical chemical process, but potassium permanganate is continuously regenerated by electro-oxidation of potassium manganate generated during the process. This leads to appreciable decrease of potassium permanganate consumption, the ratio of reactants being higher: Q: $KMnO_4$ = 1 – 3: 1kg/kg.

Previous studies have shown that Mn^{7+} regeneration on platinum electrode is possible both in the absence [10] and presence of quinoxaline [11]. The price of an electrolyser equipped with such an electrode is very high and finding a cheaper material for manufacturing of the anode, while maintaining the platinum performance, constitutes a strong issue for the process at hand.

This paper shows the results obtained through cyclic voltammetry in the study of the Mn^{6+}/Mn^{7+} couple behaviour on nickel electrode as well as the manufacturing of the laboratory electrolyser made with perforated nickel plate electrode for PDCA synthesis using electrochemically regenerated potassium permanganate as chemical reagent.

RESULTS AND DISCUSSION

The Mn^{7+}/Mn^{6+} redox couple behaviour in alkaline medium was studied through cyclic voltammetry. The curves obtained using the nickel anode in 4M KOH solution in the presence of manganese ions at various concentrations, are shown in figure 1.

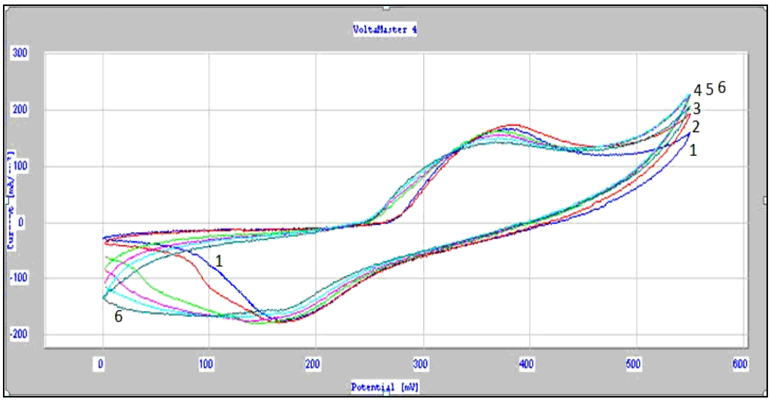

Figure 1. Cyclic voltammograms at different concentration (M) of Mn^{6+}: 0(1); $0.4\cdot10^{-3}$(2); $2\cdot10^{-3}$(3); $4\cdot10^{-3}$(4); $8\cdot10^{-3}$(5); $16\cdot10^{-3}$(6); [KOH] = 4M; 25ºC; *v* = 100 mV/s.

Cycle 1 (blue) – generated in the absence of Mn^{6+} ions – shows an anodic peak at ~ 0.38V and a cathodic peak at ~ 0.16V. The presence of the two peaks was attributed to the process:

$$2NiO(OH) + 2H_2O + 2e^- \leftrightarrow 2Ni(OH)_2 + 2OH^-$$

When metallic Ni is sunk in a NaOH solution, it gets covered with a $Ni(OH)_2$ monomolecular layer. During anodic polarization, the Ni^{2+} thus formed is converted in Ni^{3+} (NiOOH). The process is reversible and during cathodic polarization $Ni(OH)_2$ is obtained once again.

Increasing Mn^{6+} concentration (cycles 2-6) leads to a depolarization of the oxygen release and at the same time there is an observed decrease and slight displacement of the anodic peak towards more negative potentials. Another tendency towards more negative potentials is observed at the cathodic peak, starting at 0.16V. Besides this cathodic peak – present due to a reduction in Ni^{3+} – at the 0.100V potential a wave appears and increases. At an increase in Mn^{6+} ion concentration, the wave shifts significantly towards more negative potentials and the current intensity increases. The wave seems to appear as a result of the reduction in Mn^{7+} ions formed during the anodic process.

It's possible that Mn^{6+} oxidation on the nickel electrode takes place at the same time with oxygen release. During the process the color of the electrolyte solution turns from green to violet, due to $KMnO_4$ formation.

An increase in temperature from 20 to 45ºC determines the increase of the peak currents. The plots of anodic peak currents as functions of temperature and supporting electrolyte concentration for 4.10^{-3}M K_2MnO_4 are shown in figure 2.

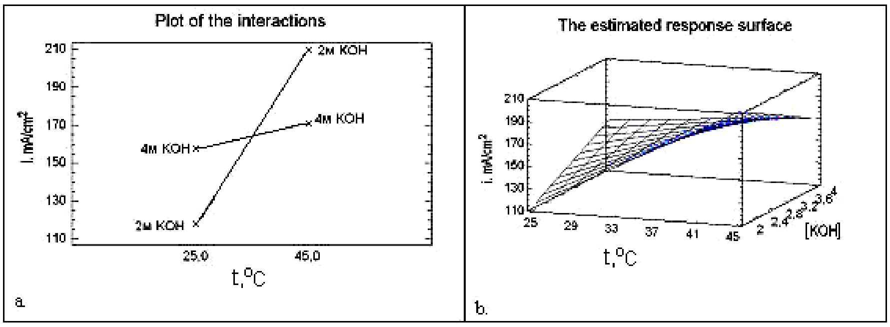

Figure 2. Anodic current density variation with temperature and supporting electrolyte concentration for 4.10^{-3}M K_2MnO_4.

The regression equation is:

$$i = -138 + 8.6 \cdot t + 69.375\,[KOH] - 1.975 \cdot t\,[KOH]$$

The cyclic voltammograms corresponding to different quinoxaline concentrations, obtained at 45°C in 2M KOH solution with $6{\cdot}10^{-2}$M $KMnO_4$, are shown in figure 3. Cycle 1, obtained in the absence of Q, the peak pair due to the $Ni^{2+} + e^- \leftrightarrow Ni^{3+}$ balance can be observed. The presence of quinoxaline in the electrolyte solution leads to a shift in the anodic peak towards more negative potentials - of up to ~ 0.30V. The intensity of this peak increases slowly with the Q concentration. The peak potential moves slowly towards more positive values as the Q concentration increases. Two peaks appear on the cathodic branch. The cathodic peak present at 0.15V – it's associated with Ni^{3+} reduction – increases with the Q concentration and moves towards more negative potentials. Next to this peak another cathodic peak can be observed, present at a potential of 0.07V. This peak also increases with Q concentration and also tents towards more negative potentials. The peak appears in the same area where Mn^{7+} ions reduction takes place.

It seems that Q oxidation can be achieved through mediated oxidation in two ways: first, using electrochemically regenerated Ni^{3+} and second, using electrochemically regenerated Mn^{7+}. The later takes place simultaneously with oxygen generation.

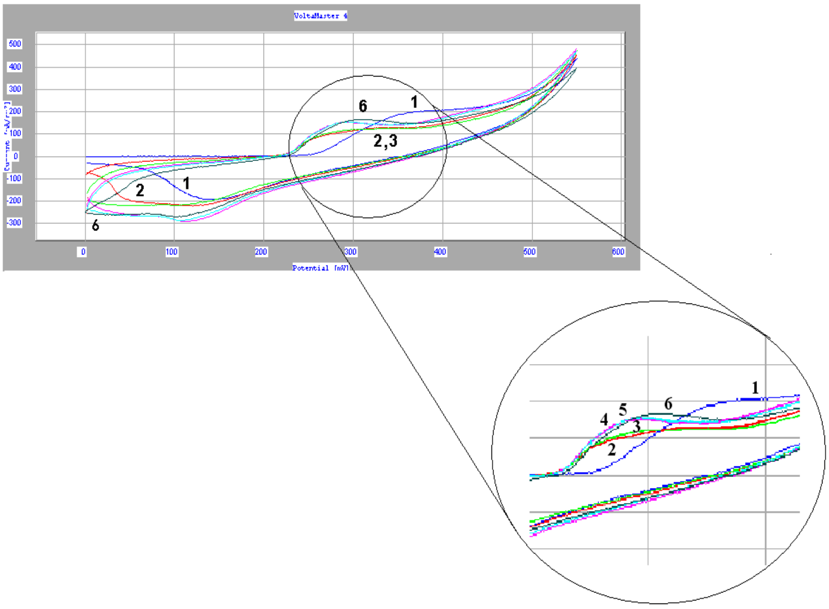

Figure 3. Cyclic voltammograms obtained for different [Q]: 0(1); $0.4{\cdot}10^{-3}$(2); $2{\cdot}10^{-3}$(3) ; $4{\cdot}10^{-3}$(4) ; $8{\cdot}10^{-3}$(5) and $16{\cdot}10^{-3}$(6) M ; t = 45°C; 2M KOH solution, $[KMnO_4] = 6{\cdot}10^{-2}$M, v = 100 mV/s.

Cyclic voltammetry studies performed at 25°C and 45°C respectively, in KOH solution containing Mn^{6+} ions, on the nickel electrode show that:

- there are several processes taking place on nickel electrode:

$$2NiO(OH) + 2H_2O + 2e^- \leftrightarrow 2Ni(OH)_2 + 2OH^-$$
$$Mn^{7+} + e^- \leftrightarrow Mn^{6+}$$

- the addition of Q in the electrolyte solution leads to a shift in the anodic peak towards negative potentials of up to ~ 0.30V. The cathodic peaks don't change when temperature is increased.
- the increase in KOH concentration, temperature, Mn^{6+} and Q concentrations favours the anodic regeneration process of Mn^{7+}.

The experimental results obtained on the nickel plate anode syntheses are shown in table 1, where: Q_{el} *– electricity quantity;* U_{med} *– cell tension;* m_{Qi} *– initial quantity of quinoxaline;* m_{Qf} *– final quantity of quinoxaline; Conv. – conversion of quinoxaline* and m_{K2PDCA} *–* K_2*PDCA quantity.*

Table 1. The experimental results for the PDCA synthesis on the nickel electrode with electrochemically regenerated $KMnO_4$.

I [A]	*i* [A/m^2]	Q_{el} [C]	U_{med} [V]	*T* [°C]	m_{Qi} [g]	m_{Qf} [g]	*Conv* [%]	m_{K2PDCA} [g]	η_s [%]	η_c [%]	*C. En.* KWh/Kg
1.8	3.5	20000	3.5	45	2	0.3	85	2.5	66.6	79.10	7.78
1.8	3.5	40000	3.5	45	2	0	100	3.2	85.2	50.62	12.15
0.9	1.7	30000	2.1	45	2	0	100	2.8	74.6	59.06	6.25
2.7	5.3	40000	3.8	45	2	0	100	2.5	66.6	39.55	16.89

- KOH concentration – 23 %
- quinoxaline concentration – 1,4 – 2,8 %
- Mn^{7+} concentration – 1,4 %.

The best results for the current yield η_c are achieved at a current density of 3.5 A/dm^2. Lower current densities lead to a higher current efficiency and a lower cell tension U_{med} – thus to a desirable lower specific energy consumption *C.En.* = 6.25 KWh/Kg. On the other hand there is a high increase in reaction time and thus a decrease in electrolyser productivity. At higher current densities (5.3 A/dm^2) the substance η_s and current efficiencies are acceptable, but energy consumption increases significantly. However, in this case, the electrolyser productivity is higher.

CONCLUSIONS

From our studies (we did not identify any similar data in the scientific literature) the regeneration of Mn^{7+} takes place on the nickel electrode even at low current densities. The presence of the final product, pyrazine-2,3-dicarboxylic acid, was confirmed through quantitative methods.

Current efficiencies of ~ 80% have been achieved at ~ 85% conversions and substance efficiencies of ~ 85% have been achieved at 100% conversions and a current efficiency of ~ 50%. Nickel constitutes a very good material for manufacturing the anode of a $KMnO_4$ regeneration electrolyser used for quinoxaline oxidation.

EXPERIMENTAL SECTION

Electrochemical cell - Cyclic voltammetry method

For the cyclic voltammetry studies we used a glass electrolysis cell (figure 4) equipped with a heating/cooling jacket and with three electrodes: the working electrode made from a nickel wire (0,008 cm^2), the platinum counter electrode (1 cm^2) and the SCE reference electrode. A PGZ 301 Dynamic-EIS Voltammetry potentiostat with VoltaMaster 4 software manufactured by Radiometer Copenhagen was also used in these studies. All electrochemical potentials mentioned in this paper are related to the SCE electrode unless otherwise specified.

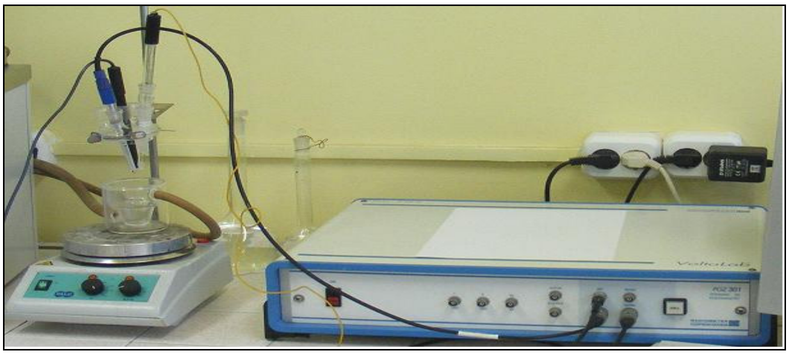

Figure 4. Electrochemical installation.

Electrolyte solution: 2 - 4M KOH (electrolyte support), K_2MnO_4 $0.4\cdot10^{-3}$ - $16\cdot10^{-3}$ M; $KMnO_4$ $2\cdot10^{-2}$ - $6\cdot10^{-2}$ M, quinoxaline $1.18\cdot10^{-2}$ – $3.62\cdot10^{-2}$ M. We used two temperatures: 25 and 45°C. The quinoxaline was from Merck, $KMnO_4$ from Riedel-de Haen and KOH, from Lach-Ner.

The method for synthesizing potassium manganate is as follows: an alkaline aqueous solution of 8N KOH containing 10g of potassium permanganate was heated at a temperature of 120°C. After the color changed from violet (Mn^{7+}) to intense green (Mn^{6+}) the supersaturated solution of Mn^{6+} was obtained. K_2MnO_4 crystals were filtered from this solution on a *S4* frit, washed with $CHCl_3$, dried and weighed, and then directly dissolved in 8N KOH solutions (25 ml measuring flask) and used in cyclic voltammetry tests.

Conductometric titration and UV-VIS Spectroscopy analysis methods were used for the quantitative determination of K_2PDCA [12], while repeated extractions with ethylic ether and evaporation to dryness followed by UV-VIS Spectroscopy were used for the quantitative determination of unreacted quinoxaline.

Laboratory electrolyser

The perforated plate electrolyser had a volume of ~ 100 ml. The perforated plate cathode and anode are shown in figures 5. The nickel anode underwent nitric acid pickling before each synthesis and between two syntheses it was washed with a mixture of sulphuric and oxalic acids.

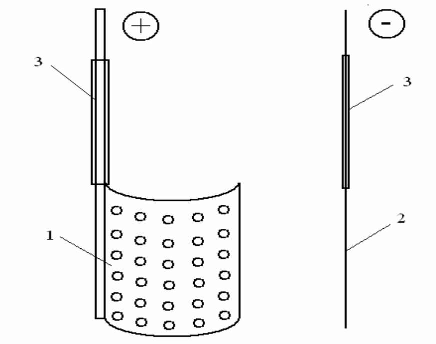

Figure 5. Components of the electrolyser used for the preliminary results of $KMnO_4$ regeneration. 1 - anode; 2 – cathode; 3 – insulating tube.

The general characteristics of the electrolyser and the working conditions are the following:

- Anodic surface, cm^2 $S_A = 0.51$
- Cathodic surface, cm^2 $S_C = 0.034$
- Sa/Sc – ratio - 15
- Electrolyte volume, ml – 90
- Current density, mA/cm^2 – 1.7 – 5.3
- Working temperature, ^{o}C – 45
- Total volume of the electrolyser, ml – 150
- anodic material – nickel perforated plate
- cathodic material – stainless steel

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REFERENCES

1. W. Wang, J.W. Lown, *Journal of Medicinal Chem*istry, **1992**, *35*(15), 2890-2896.
2. G. Reuben, G. Jones, K.C. McLaughlin, *Organic Syntheses*, **1963***, 4*, 824.
3. D. Arndt, "Manganese Compounds as Oxidizing Agents in Organic Chemistry", Open Court Publishing Co.: La Salle, IL, **1981**, 254.
4. J. March, "Advanced Organic Chemistry – Reactions, Mechanisms and Structure", 3rd Edition, *Wiley*, **1984**, 1048-1100.
5. C.A. Obafemi, W. Pfleiderer*, Helvetica Chimica Acta*, **1994**, *72,* 1549-1556.
6. H. Lund, *Journal of The Electrochemical Society*, **2002**, *149*(4), S21- S33.
7. S.A. Kotharkar, D.B. Shinde, *Journal of The Iranian Chemical Society*, **2006**, *3*(3)*,* 267-271.
8. C.A. Obafemi, W. Pfleiderer, *Helvetica Chimica Acta,* **2004**, *77*(6)*,* 1549-1556.
9. G. Reuben, G. Jones, K.C. McLaughlin, *Organic Syntheses,* **1950**, *30*, 86.
10. I. Popa, A. Dragos, I. Taranu, M. Stefanuț, C. Vaszilcsin, D. Buzatu, *Scientific Bulletin of UPT, Series of Chemistry and Environmental Engineering*, **2007**, *52*(66)*,* 1-2*,* 99-103.
11. A. Dragoş, I. Popa, I. Taranu, *New Trends and Strategies in the Chemistry of Advanced Materials with Relevance in Biological Systems, Technique and Environmental Protection,* Timişoara, 8 - 9 November **2007**, 28.
12. Țăranu B., Vlaia V., Stefănuț M., Vlătănescu N., Dobrescu M., Popa I., Analysis Methods in Obtaining Pyrazine-2,3-Dicarboxylic Acid Through Electrochemical Oxidation of Quinoxaline, *Environmental Engineering and Management Journal, "Gheorghe Asachi" Technical University of Iasi*, Romania, **2010**, *9*(8), 1115-1120.