

Electrochemical treatment of aqueous solutions containing urea

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Abstract Investigations on the anodic decomposition of urea using Ti/Pt and Ti/(RuO₂-TiO₂)_{40:60} electrodes were carried out. The kinetics of the process were examined in a periodic electrolyser. The effect of anodic current density, initial urea concentration, and sodium chloride concentration on the effectiveness of the basic process (average rate of urea decomposition, current efficiency, and unit power consumption) is discussed. When a Ti/Pt electrode is applied for urea removal from aqueous solution urea is not decomposed directly at the surface of the electrode, but rather in the bulk of the solution by hypochlorite formed during the process. When the Ti/(RuO₂-TiO₂)_{40:60} electrode is used for the removal of urea from aqueous solutions, the reaction of urea with chlorine adsorbed at the electrode predominates. In both cases non-toxic products of urea decomposition (N₂, CO₂) are formed. Comparison of the effectiveness of anodic decomposition of urea for the Ti/Pt and Ti/(RuO₂-TiO₂)_{40:60} electrodes in the periodic electrolyser at optimum process parameters has revealed that the former electrode is more favorable.

Keywords Urea · Anode material ·
Electrochemical oxidation · Wastewater treatment

1 Introduction

The industrial synthesis of urea consists in the reaction of ammonia and carbon dioxide under high pressure ($p = 10$ –

25 MPa) and temperature ($T = 420$ – 480 K). This process may be divided into the following stages: synthesis, separation of the post-reaction mixture, concentration of the urea solution, urea crystallization and granulation. In the course of urea production a large amount of wastewaters of varying urea concentrations is formed. Those wastewaters are most often purified by hydrolysis of urea [1, 2], but also other methods of removal exist: adsorption, biological decomposition, chemical oxidation, and enzymatic decomposition [3–7]. However, these methods are still under investigations and some of them require the application of complicated equipment or lead to high energy consumption, so that they cannot be applied industrially.

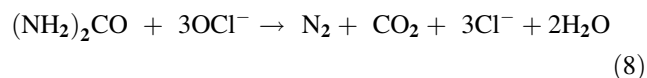
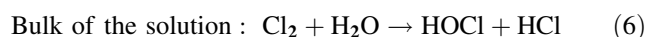
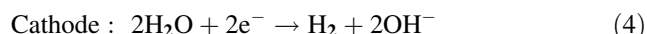
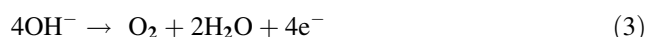
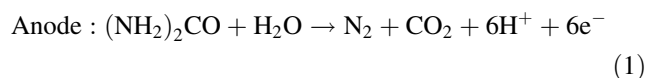
An alternative way of treating wastewaters arising in the course of the production of urea is anodic oxidation, yielding non-toxic products (CO₂, N₂, H₂O). Electrochemical methods present a modern trend in wastewater treatment, favorable to the environment and eliminating in many cases the formation of additional wastewater or, at least, decreasing their formation. Moreover, they are highly selective. Electrochemical methods can be used for the neutralization of cyanides [8, 9], phenols [10, 11], chlorophenols [12–14], trichloroethylene [15], herbicides [16], poorly-degradable organic compounds [17], landfill leachate [18], and others. Electrochemical wastewater treatment can also be successfully applied in tanneries [19–21], olive-oil production plants [22], textile industry [23–27], and in distilleries [28]. The process of electrochemical decomposition of urea on dimensionally stable electrodes covered with ruthenium and titanium oxides has been applied for the purification of dairy manure lagoon water [29].

The electrochemical oxidation of urea has been intensively investigated in attempts to use it for regeneration of dialysate in artificial kidneys [30–33]. Buffered solutions

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of the urea concentration corresponding to that of dialysates and either the platinum electrodes or electrodes made of titanium covered with ruthenium and titanium oxides have been applied for that purpose. It has been found that urea can be oxidized to such non-toxic products as N_2 and CO_2 .

During the electrolysis of the solutions containing urea and chloride ions the following reactions may occur [34–36]:



No matter if urea is oxidized directly on the anode at elevated potentials or indirectly by means of OCl^- ions its major oxidation products are nitrogen and carbon dioxide. On the basis of the investigations concerning the direct oxidation of urea performed by an in situ method it has been found that irreversible adsorption of urea molecules takes place at the surface of the electrode both in acidic and in alkaline solutions. In an acidic medium the urea molecule is adsorbed at the surface through the nitrogen atom, and in an alkaline medium—first through one of the two NH_2 -groups and then, at increased potential, through the oxygen atom [37]. In the range of potentials from 0.6 to 3.0 V, in the absence of NaCl, two adsorption maxima of urea have been observed: the first one at potential of 1.0–1.2 V, the other starting at 2.2 V and extending up to 2.8 V. Testing the adsorption of urea on a Pt electrode in a solution containing chlorides it has been found that urea causes a reduction in the adsorption of Cl^- ions. In contrast the presence of chloride ions does not affect the urea adsorption up to a potential of 1.8 V. At higher potentials the sorption of urea may compete with the adsorption of the products resulting from the oxidation of Cl^- ions on the Pt electrode. Below 1.6 V the first chemisorbed form of urea is oxidized. The oxidation currents are, however, negligible and the reaction products remain in the solution. It has been found that urea adsorption on the surface of the electrode is not the limiting stage and that the rate of that process is limited by the reaction of the chemisorbed urea with the OH radical, formed by decomposition of water. At potentials exceeding 1.7 V,

urea distinctly restricts the evolution of oxygen. At the conditions under which water decomposition does not occur and at sufficiently high potentials urea is oxidized to CO_2 and N_2 . Analysis of the polarization curves obtained in solutions of urea containing sodium chloride shows that at high potentials urea is oxidized directly on Pt without the participation of Cl^- ions [34, 35, 38]. In contrast, it was shown that during the electrolysis of a solution of urea of concentration corresponding to that of spent dialysate urea is oxidized by anodically formed chlorine. In the course of this process urea is chlorinated in the layer adjacent to the anode, first to monochlorourea, and then to dichlorourea, which again is decomposed in the bulk of the solution by the hypochlorite forming in this process [33]. The main products are: CO_2 and N_2 (resulting from the oxidation of urea), O_2 (resulting from the electrolysis of water) and H_2 formed on the cathode. The oxidation of urea by hypochlorite is a process comprising several steps, yielding such intermediate products as hydrazine and monochlorourea. It is generally supposed that the urea-hypochlorite reaction occurs in compliance with the Hoffmann reaction mechanism [39]. However, most investigations have been carried out using potentiostatic techniques, with the application of platinum electrodes of a small surface area. Anodic oxidation of urea is a rather complicated process depending on potential, the kind of anode material, the type and concentration of the base electrolyte, the concentration of urea as well as pH and temperature of the solution. Depending on the conditions of the process, various final products of the urea decomposition are obtained: CO_2 , N_2 , H_2 , CNO^- , NO_3^- , NO_2^- , $[N_2O_2]^-$, N_2O , NO_2 , $NH_2CONH_2^+$. Preliminary investigations, confirming the possibility of applying the electrochemical method in the treatment of wastewaters resulting from the production of urea have been performed making use of titanium electrodes covered with platinum and iridium as well as tantalum and iridium oxides [40].

The aim of the present report is to check the possibility of applying the Ti/Pt and Ti/(RuO_2 - TiO_2)_{60:40} electrodes for removing urea from aqueous solutions and to determine the effect of the process parameters: anodic current density, the initial urea concentration, and sodium chloride concentration, on the effectiveness and course of the anodic decomposition of urea.

2 Materials and methods

The electrolysis was carried out in a 1.5-L electrolyser made of polymethylmethacrylate. Two cathodes made of a platinum coated titanium grid were placed inside the cell and separated by the anode. The gap between the anode and cathodes was 6 mm. The anodes used were: Ti/Pt with

surface area of 1.1 dm² and Ti/(RuO₂-TiO₂)_{60:40} of surface area of 1.5 dm². The Ti/Pt electrode was made by Pt electrodeposition [41–43]. The Ti/(RuO₂-TiO₂)_{60:40} electrodes were prepared by thermal decomposition of appropriate salts on titanium [44–46]. Solutions were agitated by gases evolving on the electrodes.

The electrochemical decomposition of urea was conducted at constant current for 3 h. Samples of the electrolysed solution were collected at fixed intervals of time to determine pH, urea concentration and hypochlorite concentration. Urea was analyzed spectrophotometrically [47], while hypochlorite iodometrically [48]. Continuous measurements of the voltage drop, current and temperature of the electrolyte with the accuracy of ±0.1 V, ±0.1 A, ±0.1 K, respectively, were carried out.

The results of the above measurements were used to calculate the following parameters characterizing the process of electrochemical decomposition of urea:

- average rate of urea decomposition:

$$a = \frac{\sum m_{ri}}{\tau s} [\text{gh}^{-1} \text{dm}^{-2}] \tag{9}$$

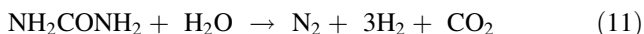
where $\sum m_{ri}$ —weight of urea decomposed in time τ ; m_{ri} —weight of urea decomposed in time $\Delta\tau$;

$$m_{ri} = V_r(c_{Ui-1} - c_{Ui})[\text{g}] \tag{10}$$

where τ —electrolysis time; s —electrode surface area; $(c_{Ui-1} - c_{Ui})$ —change in urea concentration over time $\Delta\tau$; V_r —volume of urea solution

The average rate of urea decomposition was defined as the decrease in urea weight during the unit time per the unit electrode surface area. The average rate defined in the above manner is formally based on mass balance of the system. Therefore, no correction for temperature was required.

- current efficiency related to the total urea decomposition reaction:



$$\eta = \frac{\sum m_{ri}}{m_t} \tag{12}$$

$$m_t = m_h I \tau = \frac{M}{n F} I \tau [\text{g}] \tag{13}$$

where m_t —theoretical weight of decomposed urea; m_h —electrochemical equivalent; M —molar mass of urea, 60.06 g mol⁻¹; I —current intensity; n —number of electrons exchanged (reaction 3), $n = 6$; F —Faraday constant, 96,487 C mol⁻¹; unit DC power consumption.

$$Z_j = \frac{\overline{E}_Z}{\eta m_h} [\text{kWh kg}^{-1}] \tag{14}$$

where \overline{E}_Z —average voltage drop.

The experiments were designed to determine the effect of anodic current density ($j = 2\text{--}10 \text{ A dm}^{-2}$), initial concentration of urea ($c_{0U} = 1\text{--}10 \text{ g L}^{-1}$) and concentration of sodium chloride ($c_{\text{NaCl}} = 1\text{--}10 \text{ g L}^{-1}$) on the process effectiveness (a, η, Z_j). In addition, a set of experiments was performed to check the reproducibility of the measurements.

All solutions were prepared using analytical reagent grade chemicals manufactured by POCh Gliwice, Poland and deionized water produced by a Millipore Milli-Q system.

3 Results and discussion

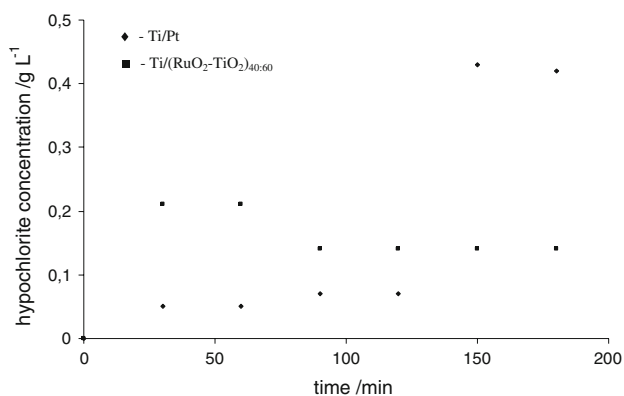
3.1 Influence of anodic current density on the rate of urea decomposition

At the Ti/Pt electrode the rate of anodic decomposition of urea was found to depend strongly on current density. An increase from 2 to 10 A dm⁻² caused an increase in the average rate of urea decomposition from 0.85 to 2.94 g h⁻¹ dm⁻² and the increase in unit power consumption from 7.85 to 16.75 kWh kg⁻¹ (Table 1). At the same time current efficiency decreased by more than two times. At 2 and 4 A dm⁻², NO₂⁻ and NO₃⁻ ions were found, which indicates an excessive oxidation of urea and precludes industrial application of that process since these ions are harmful contaminants of water. The current efficiency at 2 and 4 A dm⁻² exceeded 1, when Eq. 12 was applied for η determination (see Table 1). In this case urea may be oxidized by possibly formed hydroxyl radicals on the anode and nitrites or nitrates may be produced. The process was accompanied by a drastic increase in solution temperature, from 298 to approx. 363 K, being roughly constant after 20 min. At the end of the process, when the urea concentration reached its lowest values, the concentration of hypochlorite in the solution increased (Fig. 1). This may indicate that, urea is decomposed by hypochlorite in the bulk of the solution and explains the absence of hypochlorite during urea oxidation.

For the Ti/(RuO₂-TiO₂)_{60:40} electrode an increase in anodic current density lead to a considerable increase in the process rate. The average rate of urea decomposition increased from 0.69 to 1.97 g h⁻¹ dm⁻² while current efficiency decreased from 0.93 to 0.53 (Table 1). At the same time the unit power consumption increased more than two times (from 8.99 to 22.08 kWh kg⁻¹). The average rate of urea decomposition and the current efficiency are lower than those for the Ti/Pt electrode under the same conditions. The concentration of chloride ions did not

Table 1 Process parameters for anodic decomposition of urea using the investigated electrodes

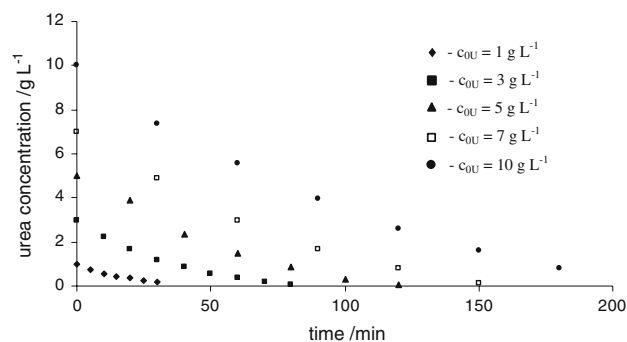
| | Ti/Pt | | | Ti/(RuO ₂ -TiO ₂) _{40:60} | | |
|--------------------------------------|--|------|--------------------------------------|---|------|--------------------------------------|
| | a/g h ⁻¹ dm ⁻² | η | Z _j /kWh kg ⁻¹ | a/g h ⁻¹ dm ⁻² | η | Z _j /kWh kg ⁻¹ |
| j/A dm ⁻² | c _{0U} = 10 g L ⁻¹ , c _{NaCl} = 5 g L ⁻¹ , τ = 180 min | | | | | |
| 2 | 0.85 | 1.15 | 7.85 | 0.69 | 0.93 | 8.99 |
| 4 | 1.74 | 1.16 | 9.02 | 1.15 | 0.77 | 13.25 |
| 6 | – | – | – | 1.48 | 0.66 | 16.45 |
| 8 | 2.70 | 0.90 | 13.64 | 1.87 | 0.63 | 17.98 |
| 10 | 2.90 | 0.78 | 16.75 | 1.97 | 0.53 | 22.08 |
| c _{0U} /g L ⁻¹ | j = 8 A dm ⁻² , c _{NaCl} = 5 g L ⁻¹ | | | | | |
| 1 | 1.35 | 0.45 | 32.80 | 1.59 | 0.53 | 22.69 |
| 3 | 2.16 | 0.72 | 16.55 | 1.98 | 0.66 | 18.15 |
| 5 | 2.20 | 0.73 | 15.16 | 1.91 | 0.64 | 15.99 |
| 7 | 2.42 | 0.81 | 15.68 | 1.93 | 0.65 | 14.73 |
| 10 | 2.70 | 0.90 | 13.64 | 1.65 | 0.55 | 16.44 |
| c _{NaCl} /g L ⁻¹ | c _{0U} = 5 g L ⁻¹ , j = 8 A dm ⁻² , τ = 180 min | | | | | |
| 1 | 2.25 | 0.75 | 22.58 | 1.90 | 0.64 | 20.09 |
| 3 | 2.62 | 0.88 | 15.70 | 1.87 | 0.63 | 17.98 |
| 5 | 2.71 | 0.91 | 13.49 | 1.91 | 0.64 | 15.99 |
| 7 | 2.84 | 0.95 | 12.21 | 1.93 | 0.65 | 14.73 |
| 10 | 2.83 | 0.95 | 11.36 | 1.65 | 0.55 | 16.44 |

**Fig. 1** Example of the variation of hypochlorite concentration; c_{0U} = 10 g L⁻¹, c_{NaCl} = 5 g L⁻¹, j = 8 A dm⁻², τ = 180 min

change significantly, which suggests no hypochlorite formation and direct urea oxidation at the electrode surface.

3.2 Influence of initial urea concentration on its decomposition rate

In the case of the Ti/Pt electrode an increase in the initial concentration of urea from 1 to 10 g L⁻¹ caused a 2-fold increase of the process rate (Fig. 2, Table 1). The current efficiency of the process also increased (from 0.45 to 0.90). The increase in initial concentration of urea decreased the unit power consumption from 32.80 to 13.64 kWh kg⁻¹. Irrespective of the initial urea concentration, the

**Fig. 2** Urea decay at varying initial urea concentration for the Ti/Pt electrode; j = 8 A dm⁻², c_{NaCl} = 5 g L⁻¹

concentration of chloride ions decreased and the concentration of hypochlorite increased during the process when the concentration of urea reached the lowest values (Fig. 1).

For the Ti/(RuO₂-TiO₂)_{60:40} electrode the rate of anodic decomposition increased with increase in urea concentration (Fig. 3, Table 1). The current efficiency of the process practically did not change with increase in the initial concentration of urea; at the same time the unit power consumption decreased from 22.69 to 16.44 kWh kg⁻¹. The decrease in urea concentration during the process to approx. 0.3 g L⁻¹ caused no change in hypochlorite concentration. This indicates that urea was decomposed on the surface of the electrode by adsorbed chlorine.

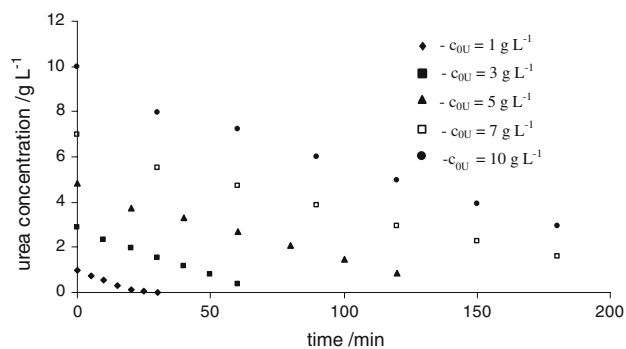


Fig. 3 Urea decay at varying initial urea concentration for the Ti/(RuO₂-TiO₂)_{40:60} electrode; $j = 8 \text{ A dm}^{-2}$, $c_{\text{NaCl}} = 5 \text{ g L}^{-1}$

3.3 Influence of sodium chloride concentration on the rate of urea decomposition

The concentration of sodium chloride negligibly affects the rate of the process (Fig. 4) when applying the Ti/Pt electrode. The average rate of urea decomposition and current efficiency increased with increase in the concentration of sodium chloride. A significant decrease was observed for the unit power consumption (from 22.58 to 11.36 kWh kg⁻¹) which may be related to the increase in solution conductivity. When the urea concentration was lower than approx. 0.3 g dm⁻³ an increase in the hypochlorite content was observed (Fig. 5). Moreover, it was observed that the higher sodium chloride concentration, the bigger was the increase in hypochlorite concentration.

With the Ti/(RuO₂-TiO₂)_{60:40} electrode an increase in sodium chloride concentration led to a decrease in the unit power consumption (Table 1). The unit power consumption decreased from 20.09 to 16.44 kWh kg⁻¹. The increase in sodium chloride increased the conductivity of the solution which consequently decreased the voltage drop and the unit power consumption. The average rate and current efficiency of the process practically did not change with increase in concentration of sodium chloride (Fig. 6,

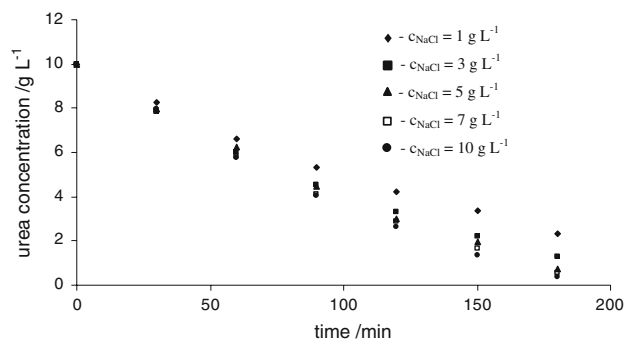


Fig. 4 Urea curves at varying NaCl concentration for the Ti/Pt electrode; $c_{0\text{U}} = 10 \text{ g L}^{-1}$, $j = 8 \text{ A dm}^{-2}$, $\tau = 180 \text{ min}$

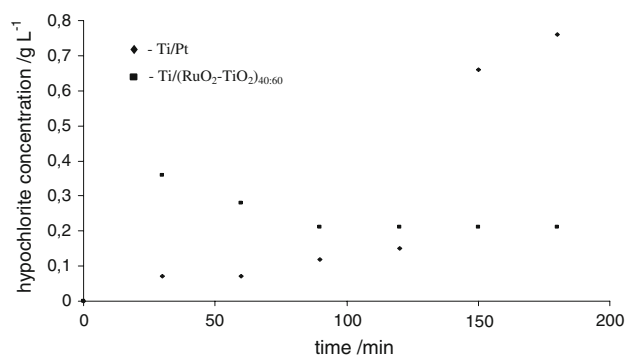


Fig. 5 Example of the variation of hypochlorite concentration; $c_{0\text{U}} = 10 \text{ g L}^{-1}$, $c_{\text{NaCl}} = 10 \text{ g L}^{-1}$, $j = 8 \text{ A dm}^{-2}$, $\tau = 180 \text{ min}$

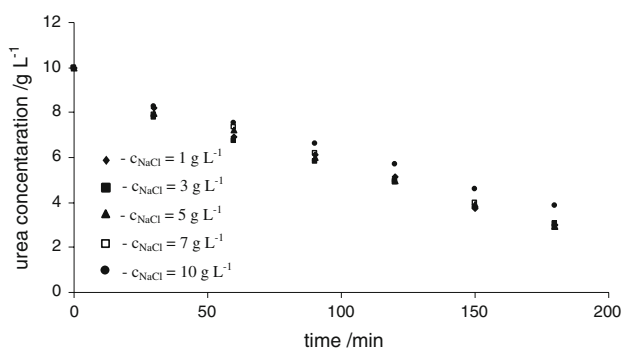


Fig. 6 Urea decay curves at varying NaCl concentration for the Ti/(RuO₂-TiO₂)_{40:60} electrode; $c_{0\text{U}} = 10 \text{ g L}^{-1}$, $j = 8 \text{ A dm}^{-2}$, $\tau = 180 \text{ min}$

Table 1). During the process the concentration of chloride ions and hypochlorite remained constant (Fig. 5). An increase in sodium chloride concentration in the solution may cause an increase in the amount of chlorine adsorbed at the electrode surface which might react with urea resulting in its decomposition.

The anodic oxidation of urea in the solutions containing chloride ions may be the result of: direct electrode reaction, oxidation by anodically produced chlorine, oxidation by chlorine adsorbed at the electrode or simultaneously of the above [33]. The predominance of one mechanism of electrochemical urea decomposition over the others and the type of products of decomposition depends on factors such as: anode material, type and concentration of electrolyte and process parameters. When the Ti/Pt electrode was used, urea was decomposed in the bulk of the solution, primarily to non-toxic products (N₂, CO₂) by hypochlorite produced during the process, but not directly on the anode surface [49]. The results confirmed the findings of previous investigations on anodic decomposition of urea carried out on this anode material and proved that urea did not undergo a direct electrochemical decomposition. The course of urea decomposition by hypochlorite in the entire volume of the

solution was also confirmed by non-linear dependence $c_M = f(\tau)$ obtained for various initial concentrations of urea (Fig. 2).

When the Ti/(RuO₂-TiO₂)_{40:60} electrode was applied to the removal of urea from aqueous solutions, urea reaction with chlorine adsorbed at the electrode gave predominantly non-toxic products (N₂, CO₂) [50]. The rate of urea decomposition did not depend significantly on its concentration in the solution which is confirmed by the linear dependence $c_M = f(\tau)$ obtained for different initial concentrations of urea (Fig. 3). The lines also showed that the reaction of urea decomposition took place directly at the anode.

3.4 The reproducibility of anodic urea decomposition

The reproducibility of anodic urea decomposition using the Ti/Pt and Ti/(RuO₂-TiO₂)_{40:60} electrodes was also examined. For that purpose the experiments were repeated (Table 2) [51]. The low values of variance (S_x^2) and standard deviation (S_x) indicate that the experiments were fully reproducible.

4 Conclusions

The investigations on the kinetics of anodic decomposition of urea in a periodic electrolyser on the Ti/Pt electrode have given the following results:

- urea is oxidized to nitrate(III) and (V) ions at current density lower than 4 A dm⁻² which excludes the possibility of application of low current densities in anodic decomposition of urea,
- the reaction of urea and chlorine produced during the process predominates the anodic decomposition of urea. It takes place in the entire volume of the solution,
- non-toxic N₂, CO₂, are major products of anodic decomposition of urea,

- Ti/Pt anode may be applied for the removal of urea from aqueous solutions by the electrochemical method on an industrial scale,
- A current density of 8 A dm⁻² and sodium chloride concentration of 5 g L⁻¹ are the optimum process parameters.

The investigations of the kinetics of anodic decomposition of urea in a periodic electrolyser on the Ti/(RuO₂-TiO₂)_{40:60} electrode have given the following results:

- urea reaction with chlorine adsorbed on the surface of the electrode predominates the anodic decomposition of urea,
- non-toxic gases: N₂, CO₂, are the major products of anodic decomposition,
- a Ti/(RuO₂-TiO₂)_{40:60} anode may be applied for the removal of urea from aqueous solutions by the electrochemical method,
- a current density of 8 A dm⁻² and sodium chloride concentration of 5 g L⁻¹ are the optimum process parameters.

The comparison of the effectiveness of the process for the Ti/Pt and Ti/(RuO₂-TiO₂)_{40:60} electrodes in the periodic electrolyser at optimum process parameters has revealed that the former electrode is more favorable.

The application of the process is connected with the necessity of using sodium chloride, which must be later removed from the purified solution. Sodium chloride can be removed by membrane processes, e.g., applying reverse osmosis or electrodialysis. In the case of reverse osmosis the solution must be preliminarily purified in order to prevent fouling of the membranes. If electrodialysis is applied, such a problem does not exist. Electrodialysis permits the reduction of the concentration of sodium chloride to acceptable levels according to legal water conventions, specific for the site in which the given industrial plant is situated. The sodium chloride may also be concentrated and recycled to the process of urea electro-

Table 2 Analysis of the reproducibility, $c_{0U} = 5 \text{ g L}^{-1}$, $c_{NaCl} = 5 \text{ g L}^{-1}$, $j = 8 \text{ A dm}^{-2}$, $\tau = 180 \text{ min}$

| Measurement number | Ti/Pt | | | Ti/(RuO ₂ -TiO ₂) _{40:60} | | |
|--|--------------------------------------|--------|--------------------------------------|---|--------|--------------------------------------|
| | a/g h ⁻¹ dm ⁻² | η | Z _j /kWh kg ⁻¹ | a/g h ⁻¹ dm ⁻² | η | Z _j /kWh kg ⁻¹ |
| 1 | 2.71 | 0.91 | 13.49 | 1.91 | 0.64 | 15.99 |
| 2 | 2.68 | 0.92 | 13.46 | 1.88 | 0.68 | 16.05 |
| 3 | 2.7 | 0.91 | 13.54 | 1.87 | 0.62 | 16.03 |
| 4 | 2.72 | 0.89 | 13.45 | 1.95 | 0.61 | 15.92 |
| 5 | 2.69 | 0.92 | 13.52 | 1.93 | 0.65 | 15.97 |
| \bar{x} (average values from measurements 1–5) | 2.70 | 0.91 | 13.49 | 1.91 | 0.64 | 15.99 |
| S_x^2 | 0.0003 | 0.0002 | 0.0015 | 0.0011 | 0.0008 | 0.0026 |
| S_x | 0.016 | 0.012 | 0.038 | 0.033 | 0.027 | 0.051 |

oxidation. Thus, excessive disposal of chlorides to surface water can be avoided.

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