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Electrochemical destruction of thiourea dioxide in an undivided parallel plate electrodes batch reactor

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Abstract

The paper presents the results of a study on the electrochemical destruction of pollutants present in a spent reducing bath of a textile factory. The investigations comprised the electro-oxidation of thiourea dioxide (TUD) (the main component of the reducing bath), sulphites and urea, which are formed during oxidation of TUD. The study performed in an undivided cell parallel plate electrodes reactor, using eight different anode materials under various hydrodynamic conditions, proved that electro-oxidation can be successfully applied for treatment of spent reducing baths. The best results of TUD and $SO_3{}^{2-}$ electro-oxidation were obtained with a Ti/Pt electrode, which showed electrocatalytic effect for both the compounds, indicating a possibility of their direct electro-oxidation on the anode. Destruction of TUD and $SO_3{}^{2-}$ proceeded also via indirect electro-oxidation, mediated by chlorine evolved on the anode. The process kinetics was mass transport controlled till $Re =$ 5000. No electrocatalytic effects were observed for urea with any of the tested anode materials. The elimination of urea resulted to proceed only by indirect electro-oxidation, mediated by chlorine. For elimination of urea a Ti/Pt–Ir electrode proved to be the best anode, probably due to its high efficiency in electro-oxidation of chlorides into chlorine. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thiourea dioxide; Electrochemical reactor; Direct electro-oxidation; Mediated electro-oxidation; Textile wastewater treatment

1. Introduction

Thiourea dioxide (TUD) is a reducing agent used in the process of dyeing of synthetic materials with disperse dyes [1]. The procedure of dyeing comprises two steps. In the first one the fabric undergoes dyeing in the batch-wise mode at a high temperature (135°C) or at low temperature with the addition of specific carriers. In the second step the excess of the dye, not perfectly adhering to the material, is removed by a reducing agent (sodium hydrosulphite is being commonly used), which reacts with the chromophore group of the dye. The reaction is carried out at a temperature of 70°C during 20–30 min under the condition of the excess of the reducing agent. In a novel technology [2] sodium hydrosulphite is replaced by TUD which has a much higher reduction potential.

The unreacted TUD contained in the reducing bath contributes significantly to the organic and nitrogen load of the wastewater if no pre-treatment is carried out and the bath is mixed directly with fabric rinsing water.

Our previous study [3] on the electrochemical oxidation of disperse dyes gave very encouraging results and stimulated us to carry on studies on an application

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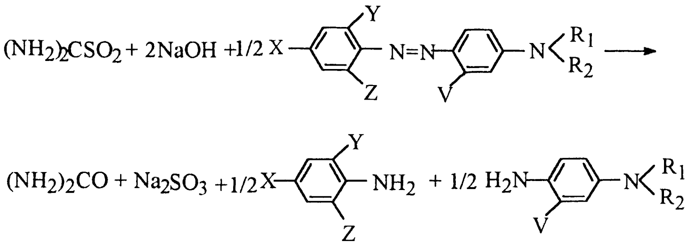
of this process also to destroy other pollutants present in textile wastewater, and particularly those deriving from the reducing bath. The present research was undertaken with the aim of checking the feasibility of electrochemical oxidation of TUD and the decomposition products it forms during reactions with dyes.

The reaction of TUD with a dye can be sketched schematically [4]:



(1)

The above reaction generates sulphites and urea. The problem related to the presence of these compounds in the spent reducing baths and the need of their elimination was encountered during the study of the electrochemical oxidation of TUD. Both sulphites and urea are known to be inhibitors of biological processes which are the means currently used for textile wastewater treatment. The investigation sets out to ascertain whether the electrochemical process can remove all the types of pollutants and whether it can provide a global solution to the problem of the pre-treatment of a spent reducing bath. For this reason experiments on the electro-oxidation of TUD were supplemented by separate tests to identify the kinetics of the elimination of sulphites and urea. The experiments designed to follow the removal of TUD, sulphites and urea included both direct and mediated electrolysis. They were conducted using eight different anodes in order to evaluate the influence of the anode material on the process kinetics and the possibility of electrocatalytic reactions. The role of hydrodynamic conditions in the performance of a reactor was also considered.

2. Experimental

The experiments were performed using three types of synthetic wastewater: (a) a solution containing 10 g dm^{-3} of TUD, prepared using the technical grade $(NH_2)_2CSO_2$ (Lorinol R by Henkel); (b) a solution containing 12 g dm^{-3} of sulphites, prepared from Na_2SO_3 (by Baker); (c) a solution containing 6 g dm^{-3} of urea, prepared from analytical grade $(NH_2)_2CO$ (by Baker). Sodium chloride (0.1 N) or sodium sulphate (0.05 N) was used as the supporting electrolyte. The experiments were performed under alkaline (pH = 9) conditions, obtained by adjusting the pH with the addition of a NaOH solution. The study was conducted in an undivided cell reactor of 0.7 dm^3 volume, equipped with a 10 × 10 cm^2 plate anode and a plate cathode (stainless steel) of the same dimensions. The anode materials which were tested included: Ti/PdO–Co_3O_4, Ti/RhO_x–TiO_2, Ti/SnO_2–Sb_2O_5, Ti/MnO_2–RuO_2, Ti/Pt–Ir, Ti/RuO_2–TiO_2, Ti/Pt and Ti/PbO_2.

A schematic view of the experimental set-up is depicted in Fig. 1.

Electrochemical oxidation was conducted under galvanostatic conditions at 2 A dm^{-2} current density. This current density has been chosen in order to operate well above the mass transport controlled cur-

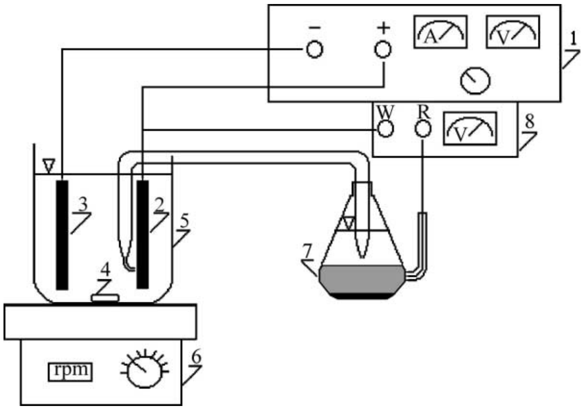


Fig. 1. Schematic view of the experimental set-up (1: DC power source, 2: anode, 3: cathode, 4: stirring bar, 5: electrochemical cell, 6: magnetic mixer, 7: SCE, 8: voltmeter).

rent density for chloride oxidation. This value would be expected to be ca. $1\,\mathrm{A\,dm^{-2}}$, considering the estimated mean mass transport rate coefficient being equal to $10^{-5}\,\mathrm{m\,s^{-1}}$ and a chloride concentration of 0.1 N. A DC stabilised power source with voltage monitoring and control in the range 1–10 V was used. The potential of the anode was monitored during the runs using, in conjunction with Luggin capillary, a home made saturated calomel reference electrode (SCE), connected to the working electrode by a high impedance voltmeter.

The influence of agitation on the performance of the electrochemical reactor was evaluated by varying hydrodynamic conditions (Reynolds number equal to 60, 250, 5000 and 8000) in the reactor equipped with the anode made of the material which gave the best performance in comparative tests.

The parameters followed during the experiments were: chemical oxygen demand (COD), determined by oxidation with dichromate and subsequent spectrophotometric determination of colour (spectrophotometer Hach DR 2000), sulphites, determined by iodometric titration, sulphates, analysed by quantitative precipitation with barium chloride, total Kjeldahl nitrogen (TKN), defined following Standards: Methods APHA (1989), pH (Orion pH-meter) and conductivity (Crison Micro CM 2200).

Cyclic voltammetric measurements pertinent to the elucidation of the electrode processes involved in the removal of pollutants were also performed. In this case the working electrodes were of $2\,\mathrm{mm^2}$ surface area. All measurements were carried out at scan rate equal to $100\,\mathrm{mV\,s^{-1}}$ and the potentials quoted against a calomel electrode (SCE) saturated with KCl. The tests were conducted for various concentrations of TUD, urea and sulphite solutions with sodium chloride or sodium sulphate as the supporting electrolyte. Cyclic voltammetric tests were performed using a 283A Model potentiostat–galvanostat (EG&G PAR) controlled with a PC via EG&G PAR 270 software.

3. Results and discussion

Under the conditions of the present study (an undivided cell reactor and a high concentration of chloride ions in the solution), two mechanisms can be responsible for the removal of pollutants: direct anodic oxidation and oxidation in the bulk solution, mediated by oxidising species formed in situ. In the former process the degree of agitation, which enhances transport of the pollutant to the anode, is expected to influence the overall removal rate.

Assuming direct anodic oxidation being responsible for its depletion, the rate of the removal of a pollutant is given by the following equation [5], valid for the conditions of diffusion limited current (that is the concentration of electroactive species at the electrode surface being zero):

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{k_\mathrm{L} A C}{V} \tag{2}$$

where C is the concentration of the pollutant ($\mathrm{mg\,dm^{-3}}$), A the surface of the anode ($\mathrm{dm^2}$), and k_L is the mass transfer coefficient ($\mathrm{m\,s^{-1}}$).

At higher potentials which were applied during experiments with the electrochemical reactor (anode potential oscillated between 2 and 3 V), an indirect electrochemical oxidation of pollutants may also occur. This is due to the oxidation of chloride and water, in which active chlorine and oxygen, respectively, are produced, giving surface mediators (e.g. $\mathrm{Cl_{ads}}^\bullet$ or $\mathrm{OH_{ads}}^\bullet$), which are continuously re-generated as soon as they are consumed by the pollutants. The anodic reactions leading to the formation of chlorine on Pt are [6]:

$$\mathrm{S + Cl^- \leftrightarrow S\text{–}Cl_{ads}{}^\bullet + e^-} \tag{3}$$

$$\mathrm{Cl^- + S\text{–}Cl_{ads}{}^\bullet \rightarrow S + Cl_2 + e^-} \tag{4}$$

Hypochlorite ions which are subsequently produced as the result of the hydrolysis of chlorine molecules can also participate in the destruction of pollutants. Another mediator which may be present in the system is H_2O_2, generated by the cathodic reduction of dissolved oxygen.

To describe bulk oxidation of pollutants, generally a pseudo-first-order chemical kinetics is used to model the process (3). It is based on an assumption that the rate of the production of the mediator and the rate of its consumption are equal (thus it does not accumulate in the system). Consequently, the following equation applies:

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = kC \tag{5}$$

where C is the concentration of the pollutant (mg dm^{-3}) and k is the apparent observed pseudo-first-order rate constant (s^{-1}).

The experiments with a solution containing TUD were performed using noble metal anodes: Ti/Pt and Ti/Pt–It only, as the other anode materials, being composed of metal oxides, were readily corroded. During the experiment with urea and sulphites, no problems were encountered, and all eight anode types could be used. In the experiments with sulphites, the following anodes were applied: Ti/RhO$_x$–TiO$_2$, Ti/MnO$_2$–RuO$_2$, Ti/Pt–Ir, Ti/RuO$_2$–TiO$_2$, and Ti/Pt.

The destruction of TUD was followed in time by the analysis of COD and sulphates. As reported above, the decomposition of TUD proceeds via generation of urea and sulphites, and consequently, during the experiments with the wastewater containing TUD, in the electrochemical reactor, along with electro-oxidation of TUD, a concomitant oxidation of in situ generated sulphites into sulphates was also expected to occur. In fact, a continuous increase of the concentration of sulphates was observed in all the runs, as can be seen from Fig. 2a.

The COD value attributed to TUD was obtained by subtracting the contribution due to sulphites from the total COD of the samples. Assuming that urea could be an intermediate of TUD electro-oxidation, in analogy to chemical oxidation, it would not be revealed by the

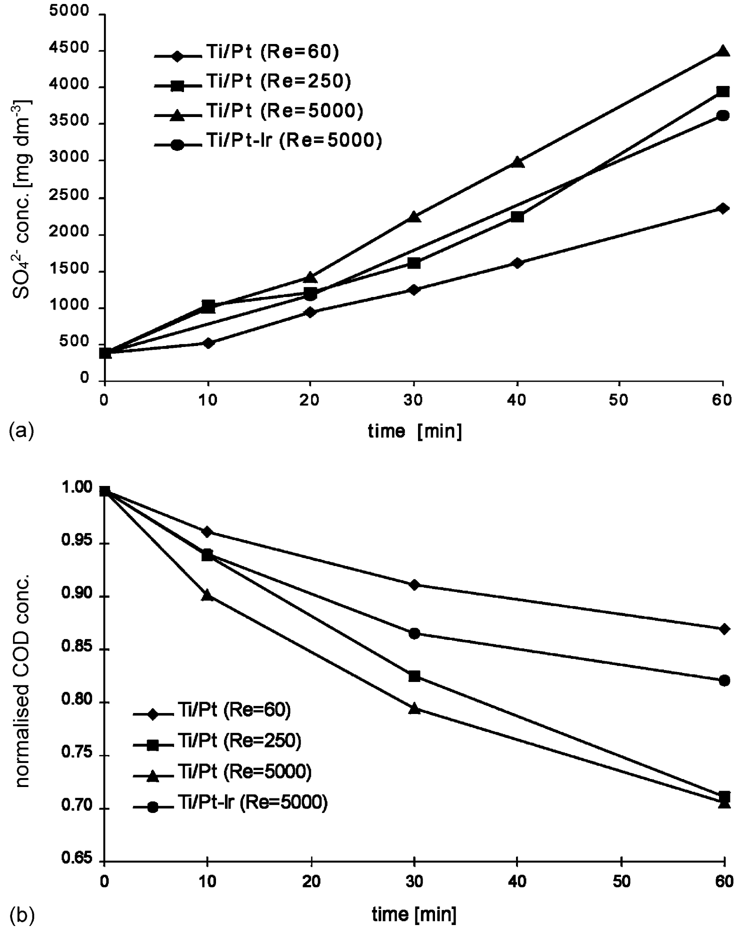


Fig. 2. Performance of the electrochemical reactor during TUD electro-oxidation; experiments with sodium chloride as supporting electrolyte; Ti/Pt–Ir and Ti/Pt anodes; (a) trend of SO$_4^{2-}$ concentration vs time; (b) trend of normalised COD values, attributed to TUD, vs time.

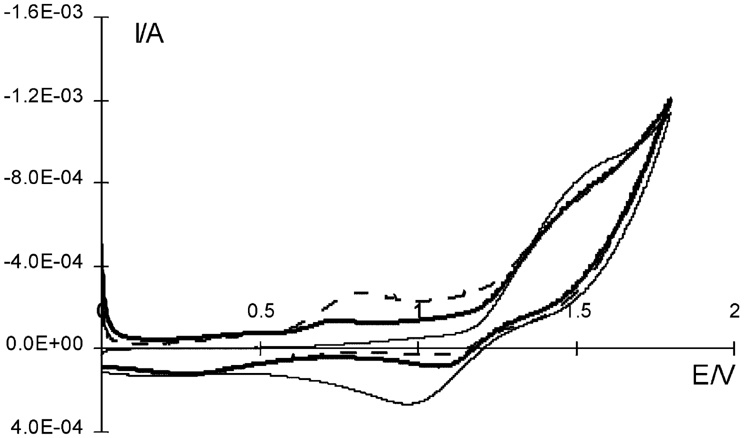


Fig. 3. Cyclic voltammograms recorded with a Ti/Pt electrode in solutions containing: (—) 7140 mg dm^{-3} of NaCl; (— bold line) 6121 mg dm^{-3} of NaCl and 740 mg dm^{-3} of TUD; (- - -) 5950 mg dm^{-3} of NaCl and 1667 mg dm^{-3} of TUD. Scan rate: 100 mV s^{-1}.

analysis of COD because under the strongly acidic conditions of COD determination it decomposes into CO_2 and NH_4^+.

The removal of COD attributed to TUD during the experiments with chloride as a supporting electrolyte is shown in Fig. 2b for both the tested anodes. The decrease of COD is depicted in terms of normalized values. Ti/Pt proved to be an excellent anode in these tests. Under the best conditions, after 1 h of the treatment, which corresponds to the passage of the charge equal to 7.2 kC, elimination of COD reached 33%. Slightly worse results were obtained while using the Ti/Pt–Ir anode.

Fig. 3 shows typical cyclic voltammograms obtained in TUD solutions and, for comparison, those obtained in the base electrolyte. During the forward scan in the base electrolyte solution, a wave around 1.5 V due to chlorine evolution [6] can be seen. On addition of TUD, another wave, located at 0.7 V, is also observed in the forward scan. The height of the latter peak is proportional to the TUD content. This suggests that direct oxidation of TUD occurs at the Ti/Pt anode. Confirmation of this fact was obtained by performing cyclic voltammetric measurements in sodium sulphate electrolyte, shown in Fig. 4, where the anodic wave at around 0.7 V was again observed.

As can be seen from Fig. 2a and b which, for the Ti/Pt anode, also compare the performance of the reactor under different hydrodynamic conditions during the removal of TUD, the degree of the turbulence significantly influenced the performance of the reactor. By increasing the degree of agitation up to 5000 *Re*, the rate of the removal of COD and the rate of formation of sulphates increased. This indicates that direct anodic oxidation might have been the prevailing process reponsible for TUD removal and under these conditions the process kinetics was mass transport controlled.

Considering that it was difficult to distinguish between chemical oxidation in the bulk and direct electro-oxidation, it was assumed that when the reaction rate was controlled by the hydrodynamic conditions, the more important process was direct anodic oxidation. Thus the removal of the pollutant can be described by Eq. (2). The values of the apparent mass transfer coefficient (k_L) calculated for the experiments related to the removal of TUD for a Ti/Pt anode and lower *Re* values ($Re = 60$, and 250) were equal to 2.91×10^{-6} and 6.76×10^{-6} m s^{-1}, respectively. It has to be noticed that in the case of the present study, k_L is a spurious parameter, as the possibility of a concomitant indirect oxidation of a pollutant is also likely.

At high turbulence, when the process was no more dependent on the degree of agitation ($Re \geq 5000$), it is likely that chemical oxidation in the bulk solution via chlorine intermediates controlled the rate of the destruction of TUD. In this case electrocatalysis

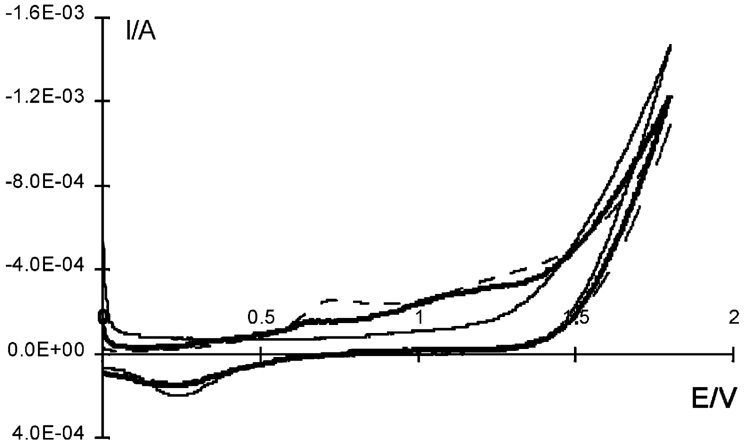


Fig. 4. Cyclic voltammograms recorded with a Ti/Pt electrode in solutions containing: (—) 8250 mg dm^{-3} of Na_2SO_4; (— bold line) 7638 mg dm^{-3} of Na_2SO_4 and 740 mg dm^{-3} of TUD; (- - -) 6875 mg dm^{-3} of Na_2SO_4 and 2000 mg dm^{-3} of TUD. Scan rate: 100 mV s^{-1}.

related to chlorine evolution gains importance. This behaviour can find a confirmation in the fact that the best results were obtained while using the Ti/Pt anode, a material known to be also a good electrocatalyst for chlorine evolution. Considering the above and also in view of the fact that in the course of electrolysis the role of direct anodic oxidation decreases due to lowering of the concentration of the pollutant, for the experiments conducted under the conditions of high turbulence, the reaction rate model based on chemical kinetics was applied (Eq. (5)). The experimental results in fact proved to follow a pseudo-first-order kinetics. The values of rate constant (k) calculated for the two tested anodes for the conditions of high turbulence ($Re \geq 5000$) are reported in Table 1, along with correlation coefficients, given in brackets. Also in this case, due to the co-participation of direct anodic oxidation, the kinetic rate constant k is a spurious parameter.

The current efficiency during the process of elimination of TUD was also calculated. Assuming a four electron reaction during COD destruction, the current efficiency η can be evaluated by [7]:

$$\eta = \frac{FV}{8I}\frac{\left[(\mathrm{COD})_t - (\mathrm{COD})_{t+\Delta t}\right]}{\Delta t} \tag{6}$$

where I is the current applied during the electrolysis (A), F the Faraday constant (96490 C mol^{-1}), V the volume of the solution under treatment (dm^3), and Δt is the time of electrolysis (s). The COD values are expressed in gO_2 dm^{-3}.

Table 1
Results of electro-oxidation of TUD, urea and sulphites

Anode material	Electro-oxidation of TUD		Electro-oxidation of urea, TKN		Electro-oxidation of SO_3^{2-}	
	COD, $k \times 10^{-4}$ (s^{-1})	SO_4^{2-}, $k \times 10^{-4}$ (s^{-1})	η (%)	$k \times 10^{-4}$ (s^{-1})	η (%)	$k \times 10^{-4}$ (s^{-1})
Ti/Pt	1.05 (0.94)	7.28 (0.93)	19	0.11 (1.00)	132	3.64 (0.87)
Ti/Pt–Ir	0.60 (0.89)	6.57 (0.95)	97	0.48 (0.89)	93	2.52 (0.88)
Ti/PdO–CO_3O_4	n.d.	n.d.	69	0.33 (0.85)	n.d.	n.d.
Ti/RhO_x–TiO_2	n.d.	n.d.	40	0.23 (0.91)	68	1.70 (0.79)
Ti/SnO_2–Sb_2O_5	n.d.	n.d.	0	n.d.	n.d.	n.d.
Ti/RuO_2–TiO_2	n.d.	n.d.	49	0.25 (0.99)	93	2.35 (0.85)
Ti/PbO_2	n.d.	n.d.	104	0.60 (0.96)	n.d.	n.d.
Ti/MnO_2–RuO_2	n.d.	n.d.	74	0.43 (0.79)	96	2.87 (0.83)

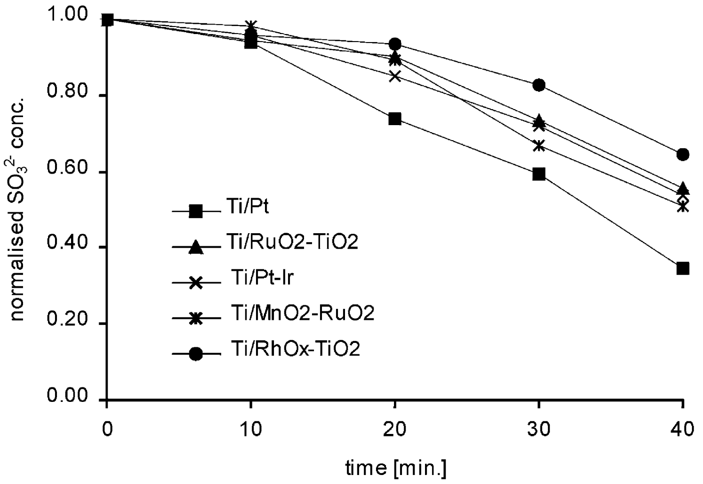


Fig. 5. Trend in normalised $SO_3{}^{2-}$ concentration in time during electro-oxidation using reactors equipped with different anode materials.

Under the conditions of high turbulence in the reactor ($Re \geq 5000$), the current efficiency for the elimination of TUD during the experiments with a Ti/Pt anode was equal to 100%.

The results of the study concerning the elimination of sulphites are presented in Fig. 5, which depicts the performance of the reactor during electrolysis of a solution containing sulphites under the conditions of the *Re* number equal to or above 5000. Regarding the removal of this pollutant, the Ti/Pt anode proved the best.

Cyclic voltammograms performed on an aqueous sulphite solution, recorded with the Ti/Pt anode, are shown in Fig. 6. Also in this case, an anodic wave around 0.5 V appears when Na_2SO_3 is added to the base electrolyte. This wave increases as the concentration of sulphites increases. This indicates that the wave belongs to sulphite oxidation. Since the sulphite oxidation wave occurs at less positive potentials than the TUD wave, it follows that at the oxidation potential of TUD also $SO_3{}^{2-}$ is concomitantly oxidised. This is also evident from the voltammogram shown

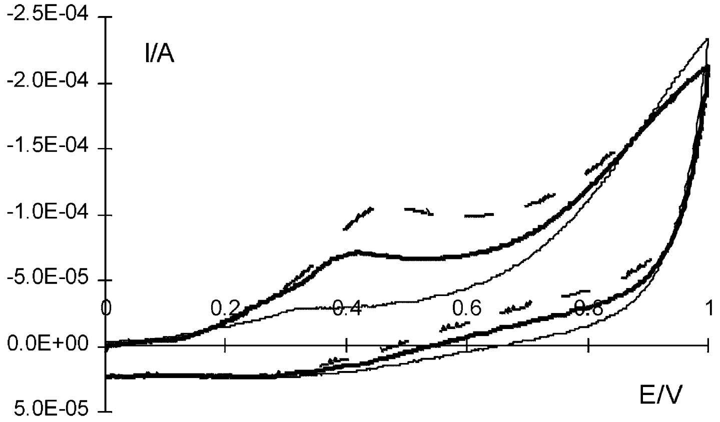


Fig. 6. Cyclic voltammograms recorded with a Ti/Pt electrode in solutions containing: (—) 7932 mg dm^{-3} of Na_2SO_4 and 461 mg dm^{-3} of Na_2SO_3; (— bold line) 7366 mg dm^{-3} of Na_2SO_4 and 1285 mg dm^{-3} of Na_2SO_3; (- - -) 6875 mg dm^{-3} of Na_2SO_4 and 2000 mg dm^{-3} of Na_2SO_3. Scan rate: 100 mV s^{-1}.

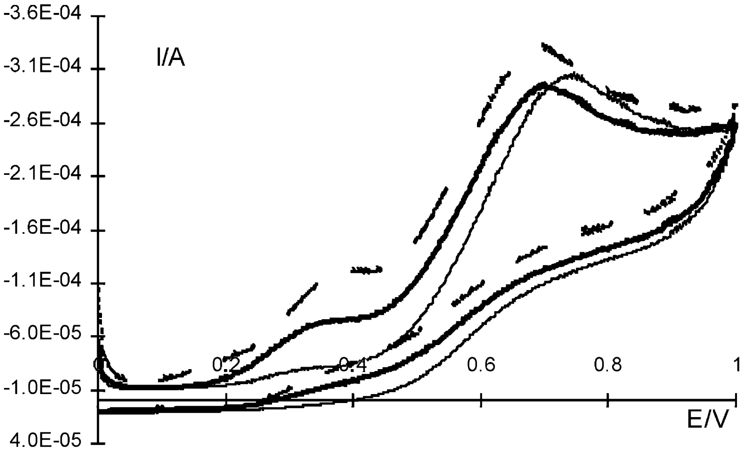


Fig. 7. Cyclic voltammograms recorded with a Ti/Pt electrode in solutions containing: (—) 5100 mg dm^{-3} of NaCl and 2850 mg dm^{-3} of TUD; (— bold line) 4697 mg dm^{-3} of NaCl, 2631 mg dm^{-3} of TUD and 947 mg dm^{-3} of Na_2SO_3; (- - -) 4353 mg dm^{-3} of NaCl, 2439 mg dm^{-3} of TUD and 1756 mg dm^{-3} of Na_2SO_3. Scan rate: 100 mV s^{-1}.

in Fig. 7, where the voltammetric behaviour of solutions containing both TUD and sulphite ions is displayed. In the tests with a Ti/Pt material as an anode, agitation had a noticeable influence on the rate of the process. Experiments of electro-oxidation of sulphites performed in a reactor equipped with this anode at the hydrodynamic conditions characterised by $Re = 250$ result in the lower rate of reaction by comparison to the tests under $Re \geq 5000$. The mass transfer coefficient calculated using Eq. (2) was in this case equal to 25.2×10^{-6} m s^{-1}.

The current efficiency and the kinetic rate constant values, which characterise the removal of sulphides, reported in Table 1, were calculated for the experimental conditions of high turbulence. Eq. (3) was used to model the kinetics of the process. The current efficiency, far exceeding in this case 100%, has to be noticed. We hypothesise that the removal of sulphites might have proceeded not only via the reaction occurring in the bulk between sulphites and active chlorine, but also with H_2O_2 produced on the cathode. This oxidising species could be formed by reduction of dissolved oxygen present in the system. This may explain the observed apparent anodic current efficiency higher than 100%.

The performance of the process during the electro-oxidation of urea was followed by the determination of TKN due to the fact that urea hydrolyses in alkaline conditions according to

$$(NH_2)_2CO + 2OH^- \rightarrow 2NH_3 + CO_3{}^{2-} \qquad (7)$$

In this reaction, ammonia is generated and it can be electro-oxidised in a direct process on the anode or via mediator such as chlorine, producing N_2 and N_2O [8–11]. No electrocatalytic effects were observed for urea or ammonia with any of the tested anode materials under the conditions of the present study. Relatively low current efficiency was obtained during the electro-oxidation of urea in the reactor equipped with most of the anodes (e.g. $\eta = 19\%$ was achieved for a Ti/Pt anode (see Table 1)). A high efficiency was reached only for Ti/Pt–Ir and Ti/PbO_2 anodes. The former one manifests high electrocatalytic properties towards chloride oxidation, as proved by Atanasoski et al. [12]. The lack of electrocatalysis indicates that the removal of the ammonium ion is accomplished by oxidation with chlorine (hypochlorite) evolved at the electrode due to the electro-oxidation of chlorides, and confirms our previous conclusions regarding elimination of this pollutant [11].

Data relative to the removal of urea modelled using Eq. (3) are presented in Table 1. It must also be considered that a partial stripping of NH_3 from the solution is very likely to occur. In fact, under the alkaline conditions of the runs and a temperature of 25°, it can be estimated that about 35% of ammonium is present in the solution in the form of free NH_3. Stripping of gaseous NH_3 is strongly enhanced by the development at the cathode of microbubbles of hydrogen. During their formation, partial pressure of NH_3 inside the bubbles is equal to zero, which makes them act as a sort of a "pump".

4. Conclusions

The study showed that elecro-oxidation is a successful method for the destruction of TUD, sulphites and urea, which are the by-products of its decomposition. The process proved feasible to be conducted in a simple undivided cell reactor equipped with parallel plate electrodes. The performance of the reactor was a function of the electrode material due to different electrocatalytic properties towards the removal of considered pollutants. The best results of TUD and SO_3^{2-} electro-oxidation were obtained with the Ti/Pt electrode, which showed electrocatalytic effect for both the compounds, indicating a possibility of their direct electro-oxidation on the anode. Destruction of TUD and SO_3^{2-} proceeded also via indirect electro-oxidation, mediated by chlorine evolved on the anode.

No electrocatalytic effects were observed for urea with any of the tested anode materials. For elimination of urea, the Ti/Pt–Ir electrode proved to be the best anode, most probably due to its high efficiency in electro-oxidation of chlorides into chlorine.

Designing the electrochemical process for the elimination of TUD, a two-step sequence should be adopted, using two different anode materials. In the first reactor, equipped with the Ti/Pt anode, TUD and sulphites are preferentially oxidised. The second step, aimed to electro-oxidise urea, should comprise a reactor equipped with the Ti/Pt–Ir anode. This material is to be preferred to the Ti/PbO_2 anode, as the latter one can be subjected to corrosion by a residual TUD eventually present in wastewater leaving the first reactor.

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