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## **ELECTROCHEMICAL REMOVAL OF NITRATE FROM WASTEWATER USING COPPER CATHODE**

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**Abstract.** Water pollution by nitrates is due to increased use of synthetic nitrogen fertilisers, live-stock manure in intensive agriculture, and industrial and municipal effluent discharge. This pollution represents a high risk for aquatic systems and human health. This is why the World Health Organisation (WHO) recommended a maximum limit of 50 mg l<sup>-1</sup> for nitrate concentration (NO<sub>3</sub><sup>-</sup>) in drinking water. The purpose of this study is nitrate removal from wastewater by electrochemical reduction using copper (Cu) cathode and platinised titanium (Pt/Ti) anode. Copper has very good electrical properties and a very high electrocatalytic activity for electrochemical cathodic reduction of nitrate. Galvanostatic batch electrolysis of synthetic nitrate wastewaters have been carried out in an undivided electrochemical cell using different nitrate and supporting electrolytes concentrations and current densities as a function of electrolysis time. The influence of these variables on removal efficiency of nitrate, current efficiency and energy consumption was reported.

*Keywords:* wastewater, nitrate, electrochemical removal, copper.

### **AIMS AND BACKGROUND**

Lately, due to a large amount of nitrate (NO<sub>3</sub><sup>-</sup>) coming from different pollution sources, increase of nitrate concentration in drinking water is noted more often. High nitrate concentration contributes to negative effects on human health and environment. Pursuant to the European Directive on quality of drinking water, maximum allowed nitrate concentration is 50 mg/l (Refs 1 and 2). Nitrate pollution sources are various and mostly represent chemical fertilisers, detergents, food industries, industrial processes in metal and electric industries, pesticides and nuclear fuels. Hence, nitrates can enter both surface and underground waters, and, consequently, the food chain as well<sup>3</sup>. Cioroi<sup>4</sup> researched nitrates contents in wells (Galati, a region in Romania) and stated that most of them contain higher nitrate concentration than the maximum allowed one.

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Nitrates ( $\text{NO}_3^-$ ) and nitrites ( $\text{NO}_2^-$ ) occur as inorganic ions in nature, which are a part of nitrogen (N) cycle. Microbe activities in land or water dissolve organic waste, which contains nitrogen, first as ammonium ( $\text{NH}_3$ ), which, afterwards, is oxidised into  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . Since  $\text{NO}_2^-$  easily oxidises into  $\text{NO}_3^-$ ,  $\text{NO}_3^-$  are compositions that mostly could be found in underground and surface waters in oxidised conditions. Compositions containing  $\text{NO}_3^-$  are generally soluble in land and migrate into underground waters.

Several different processes, including biological and chemical denitrification, reverse osmosis, electrodialyses, ion exchange processes and catalytic denitrification, could remove  $\text{NO}_3^-$  from water with various efficiency and cost efficiency levels<sup>5-9</sup>. Reduction of  $\text{NO}_3^-$  by biological denitrification requests constant monitoring such as: control of pH-value, adding carbon sources, temperature maintenance<sup>10</sup>. Extracting methods such as reverse osmoses and ion exchange cause secondary pollution, which increases costs of the process<sup>11-13</sup>.

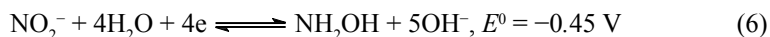
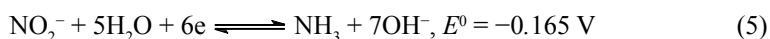
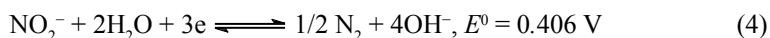
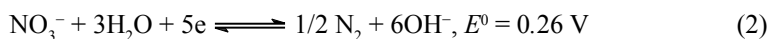
Apart from the mentioned processes, electrochemical process is effective and applicable to denitrification of waste, underground waters and drinking waters, where nitrates are turned into harmless products with help from various cathodic materials<sup>14-16</sup>. Advantages of electrochemical treatment of waste waters in comparison to conventional treatments are mainly efficiency, adapting, safety, lower costs, easy management as well as numerous recent researches focused on this method<sup>17</sup>.

There are many researches of electrochemical reduction of nitrates with different materials such as: Pt, Ni, Pb, Zn, Fe, Cu, Ti, Au, Ru, Rh, Ir, Sn, vitrous carbon, etc.<sup>16</sup>. Al, Fe and Ti electrodes showed 70–97% efficiency for nitrate reduction whereas graphite one showed only 8% of efficiency. Al and Fe electrodes transform nitrates mainly into ammonium whereas Ti electrode transforms them to nitrogen<sup>15</sup>. With and without NaCl, efficiency in removing nitrates was noted for the following series, depending on electrode material  $\text{Fe} > \text{Cu} > \text{Ti}$ . Efficiency of removing nitrates was 87% for 3 h using Fe cathode with NaCl (Ref. 14).

Electrochemical reduction of nitrates using copper and various modifications of copper electrode has been a subject of researches for many years<sup>14,18-21</sup>. Most of these researches were performed in different conditions and it is difficult to compare acquired results directly. Anyway, it was proved that copper is the fastest in reaction to reduction of nitrates<sup>21</sup>.

Some electrodes such as Cu and Fe, are known to be efficient promoters for electrochemical reduction of nitrates<sup>15,18,22,23</sup>. However, as reduction of  $\text{NO}_3^-$  ions is one of several ways for its removal from waste water, electrochemical reduction of nitrates leads to relatively broad specter of products, such as  $\text{N}_2$ ,  $\text{NH}_2\text{OH}$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ . Main cathodic reactions in electrochemical reduction of nitrates of ions to nitrogen and ammonium are presented as follows<sup>24</sup>:

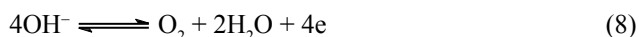




The main secondary reaction on cathode is hydrogen evolution:



The main anode reaction is oxygen evolution:

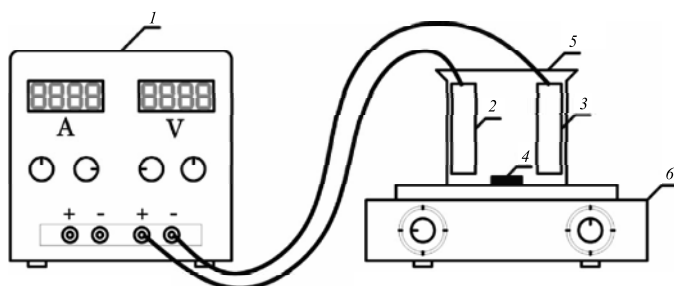


The overall electrochemical reaction is as follows:



## EXPERIMENTAL

For the purpose of experimental research, we used commercially available 99% potassium nitrate ( $\text{KNO}_3$ ), Lachner, Czech Republic and 99% sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), Lachner, Czech Republic. All the listed chemicals are of p.a. purity. As electrode material we used copper (Cu-PHC/CW020A, EN 13601:2002; min. 99.95% Cu, 0.001–0.005% P, max. 0.005% Pb, max. 0.0005% Bi) and platinised titanium (Ti – grade 2; 2.5  $\mu\text{m}$  Pt, Metakem, Germany). Electrochemical batch reactor (Fig. 1) is made of polypropylene of capacity 500  $\text{cm}^3$  with possibility of constant mixing (500 rpm/min), which contains two electrodes of the same dimensions (area). Copper cathode is made of metal sheet dimensions 50  $\times$  33.5  $\times$  1 mm. Platinised titanium anode consists of titanium based material and it is mesh type A (surface factor 1.0). Distance between electrodes was 30 mm. Electrodes were connected to digital power source (Atten, APS3005SI; 30V, 5A).



**Fig. 1.** Schematic view of electrochemical reactor

1 – source of electric power; 2 – anode; 3 – cathode; 4 – magnetic stir bar; 5 – electrochemical cell; 6 – magnetic stirrer

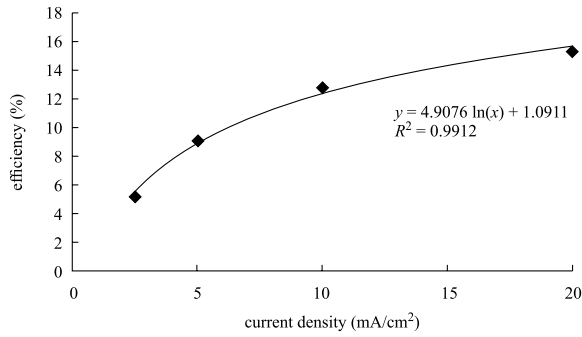
All the experiments were performed at a starting temperature of sample 25°C and 400 ml of synthetic wastewater volume. Before each treatment, current density was set at desirable value. Before each treatment, electrodes were mechanically cleaned and washed with detergent and acetone in order to remove surface grease and electrode surfaces were cleaned by emerging (5 min) in diluted (1:2) solution of HCl and HNO<sub>3</sub> before each treatment. Prepared sample of synthesised wastewater was analysed before and after the treatment for the following parameters: nitrate concentration, total dissolved solids (TDS), pH value, electrolytes resistance ( $\rho$ ) and conductivity ( $\kappa$ ). TDS,  $\rho$ , pH value,  $\kappa$  and nitrate concentration were determined in accordance with standard methods<sup>25</sup>. TDS, pH value and conductivity were determined on multi-parameter analyser (Consort C861), and measuring nitrate concentration was performed by UV/vis. spectrophotometer (Perkin Elmer, Lambda 25).

**Table 1.** Characteristics and composition of the nitrate synthetic wastewater depending on the concentration of supporting electrolyte (Na<sub>2</sub>SO<sub>4</sub>)

Na <sub>2</sub> SO <sub>4</sub> (mg l <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg l <sup>-1</sup> )	pH value	TDS (g l <sup>-1</sup> )	$\kappa$ ( $\mu$ S cm <sup>-1</sup> )	$\rho$ ( $\Omega$ cm)
0	25	6.2	0.029	82	14900
500	25	6.2	0.45	708	1520
1000	25	6.2	0.83	1389	719
2000	25	6.2	1.56	2620	382
4000	25	6.2	3.15	5210	192

## RESULTS AND DISCUSSION

In order to confirm efficiency of the copper cathode nitrates reduction from synthetically prepared waste water, researches of effects of applied current density (from 2.5 to 20 mA/cm<sup>2</sup>) to efficiency of nitrates reductions (Fig. 2) were performed first. Due to the small conductivity of synthetic waste water (Table 1), containing 25 mg/l NO<sub>3</sub><sup>-</sup>, 1 g/l Na<sub>2</sub>SO<sub>4</sub> was added as supporting electrolyte. In 30 min of treatment, at 20 mA/cm<sup>2</sup> current density, the highest efficiency was achieved amounting to 15.4%, which actually is the most often applied current density in other researches of electrochemical nitrates removal<sup>14</sup>.



**Fig. 2.** Efficiency of nitrates removal depending on applied current density ( $t = 30$  min)

Change of current density has a logarithm dependency to efficiency of nitrates removal and could be presented by the following equation:

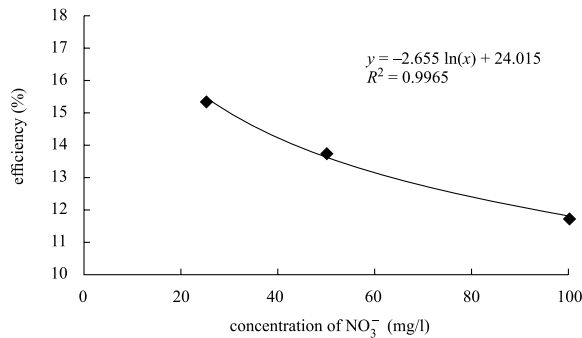
$$E = 4.9076 \ln(j) + 1.0911 \quad (10)$$

where  $E$  is the efficiency of nitrate removal and  $j$  – current density.

Figure 3 shows effect of initial concentration of nitrates with 1 g/l  $\text{Na}_2\text{SO}_4$  being supporting electrolyte, where could be noted that efficiency grows with decreasing nitrates concentration. Effect of initial concentration of nitrates to efficiency of removal could be presented by the following equation:

$$E = -2.655 \ln(\gamma_{\text{NO}_3}) + 24.015 \quad (11)$$

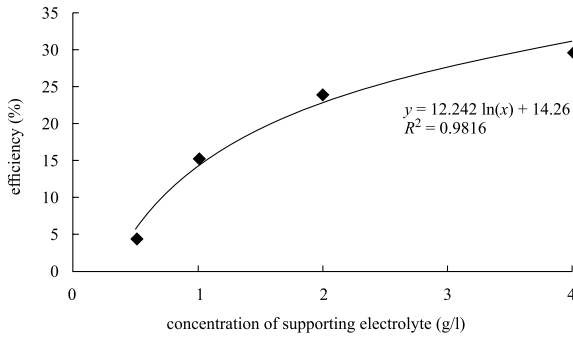
where  $\gamma$  is the mass concentration.



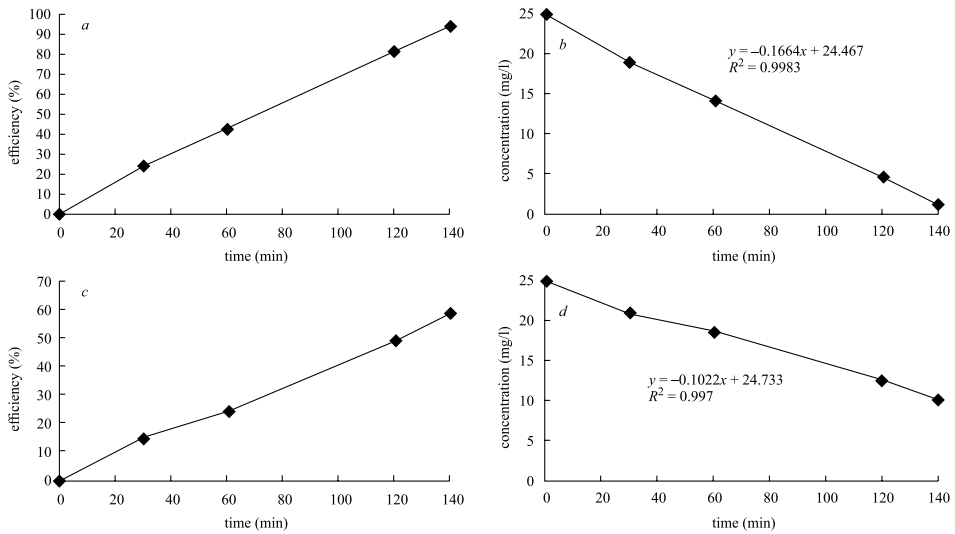
**Fig. 3.** Efficiency of nitrates removal depending on initial concentration of nitrates ( $t = 30$  min)

Due to small conductivity of synthetic waste water and increase of removal efficiency, there was testing effect of supporting electrolyte concentration, i.e. sodium-sulphate, performed (Fig. 4). Increase of concentration has logarithm dependency (12) whereas using 4 g/l  $\text{Na}_2\text{SO}_4$  we get to 29.88% efficiency of nitrates removal in 30 min.

$$E = 12.242 \ln(\gamma_{\text{Na}_2\text{SO}_4}) + 14.26 \quad (12)$$



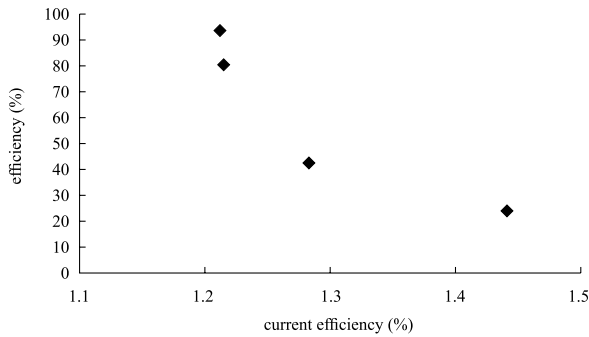
**Fig. 4.** Efficiency of nitrates removal depending on concentration of supporting electrolyte ( $\text{Na}_2\text{SO}_4$ ) with  $j = 20 \text{ mA/cm}^2$  ( $t = 30 \text{ min}$ )



**Fig. 5.** Effect of electrolysis time to electrochemical nitrates removal ( $j = 20 \text{ mA/cm}^2$ )  
*a* – effect of time to removal efficiency ( $\gamma_{\text{Na}_2\text{SO}_4} = 2 \text{ g/l}$ ); *b* – effect of time to decrease of nitrates concentration ( $\gamma_{\text{Na}_2\text{SO}_4} = 2 \text{ g/l}$ ); *c* – effect of time to removal efficiency ( $\gamma_{\text{Na}_2\text{SO}_4} = 1 \text{ g/l}$ ); *d* – effect of time to decrease of nitrates concentration ( $\gamma_{\text{Na}_2\text{SO}_4} = 1 \text{ g/l}$ )

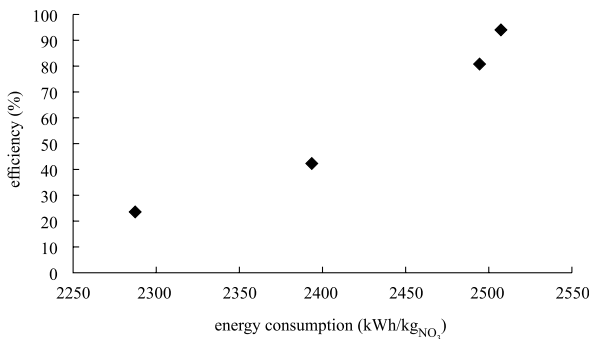
Figures 5*a* and *b* show the effect of electrolysis time to efficiency and decrease of nitrate concentration with addition of 2 g/l  $\text{Na}_2\text{SO}_4$  as support electrolyte where in 140 min almost complete nitrates removal is accomplished. It is noted that reaction of nitrates reduction of zero-order (Fig. 5*b*) with reaction rate coefficient  $k = -0.1664 \text{ mg/l min}$  whereas on other electrode materials, such as zero-valent iron (ZVI) pseudo-zero-order reaction rate, and on nanoscale-zero-valent iron (NZVI) pseudo-zero-order reaction rate<sup>26</sup>. In accordance with other available literature, electrochemical reduction of nitrates follows reactions of the first-order using aluminum, titanium, iron and graphite as electrode material<sup>15</sup>. With 1 g/l  $\text{Na}_2\text{SO}_4$  as a supporting electrolyte in 140 min efficiency is 58.85% (Figs 5*c*, *d*). In this

case, too, it is a reaction of zero-order with reaction rate coefficient  $k = -0.1022$  mg/l min. There are no researches available for kinetics of reactions with copper electrodes.



**Fig. 6.** Dependence of current efficiency on nitrates removal efficiency ( $\gamma_{\text{Na}_2\text{SO}_4} = 2$  g/l,  $j = 20$  mA/cm<sup>2</sup>)

Current efficiency depending on efficiency is low (1.21–1.44%) and it additionally falls with efficiency increase (Fig. 6). Reason for this might be a big number of possible electrochemical reactions (1)–(8) that go on in such a system, which has negative effects to current efficiency. For 94.94% efficiency we need 2506.95 kWh of electric energy per 1 kg of removed nitrate (Fig. 7).



**Fig. 7.** Dependence of energy consumption on nitrates removal efficiency ( $\gamma_{\text{Na}_2\text{SO}_4} = 2$  g/l,  $j = 20$  mA/cm<sup>2</sup>)

## CONCLUSIONS

Electrochemical removal of nitrates could successfully be performed through reduction on copper electrode. Process efficiency increases with adding sodium sulphate as supporting electrolyte, and 2 g/l are enough in order to remove nitrate almost entirely (94.94%) in 140 min of treatment. Further researches should be



focused on increasing current efficiency and decrease of electrical power consumption, which would enhance this treatment.

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*Received 10 October 2015*

*Revised 1 November 2015*