Removal of urea from industrial wastewater using electrochemical decomposition

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Abstract: In this study, experiments were carried out using a bench-scale electrochemical cell incorporating flow-by porous graphite electrodes for decomposition of urea. The effect of anodic current density, influent feed flow rate, sodium chloride concentration, and urea concentration, on basic process indices, the removal rate of urea, current efficiency, and energy consumptions, were investigated. The experimental results showed that, the removal rates of urea increased with increasing the current density; at the same time, the energy power consumption increased, and the current efficiency decreased. At initial urea concentration of 2500 ppm, maximum current efficiency is 82, maximum removal rate is 0.78 g/h, and minimum energy consumption is 11 kWh/kg.


Key words: Urea, flow-by, graphite, porous, decomposition

1. Introduction

Water is one of the abundantly available resources in nature and is essential for animal and plant life. Pollution of water bodies is increasing steadily due to industrial proliferation and urbanization.

Electrochemical waste destruction shows several benefits in terms of costs and safety. The process runs at very high electrochemical efficiency and operates essentially under the same conditions for a wide variety of wastes. Operation at room temperature and atmospheric pressure reduces the possibility of volatilization and the discharge of unreacted waste. The waste treatment can be terminated within seconds by simply cutting off power to the electrodes.

The removal of undesirable components from aqueous phases is based on choice of the appropriate electrode material and potential, or by assisting membrane systems to drive the electrode processes selectively [1].

One of the common water pollutants is urea which is usually present in wastewater discharges from several sources. Urea is not directly toxic but its hydrolysis into ammonia leads to toxicity to both animal and marine life. Urea management has been a major environmental and health issue. Human/animal urine, industrial synthesis process of urea, and dialysate used in artificial kidney, produce a large amount of wastewater with varying urea concentration. The wastewater containing urea can go through a natural conversion to ammonia, which is then emitted to the atmosphere [2].

Discharging this wastewater from urea plants and used dialysate solutions have a negative influence on the environment. Urea is considered deleterious in natural waterways since it promotes algae growth and hydrolyses slowly.

Urea was electrochemically treated in order to suppress the emission of the unpleasant odor due to ammonia, which is an end product of the hydrolysis of urea in urine by urease. As a result of the electrochemical reaction, the reactivity of urease was found to be suppressed when the potential was maintained at 240 mV vs SHE (Standard Hydrogen Electrode). Thus, urine can be stored under continuous electrochemical treatment without emitting the unpleasant ammonia odor and thus serve as toilet flush water [3].

The electrochemical treatment for urea-rich wastewater has recently become a topic of attention due to its potential applications, including wastewater remediation, hydrogen production, electrochemical sensors, and fuel cells [4-7].

Removal of urea from wastewater can be achieved by several methods including stabilization ponds, Physical-chemical, air stripping, ion exchange, and Biological methods such as activated sludge, trickling filters, and oxidation ditches but anodic oxidation of urea has several advantages over
other techniques. The anodic oxidation does not need to add a large amounts of chemicals to wastewater or to feed O₂ to cathode, with no tendency of producing secondary pollution and fewer accessories required. These advantages make anodic oxidation more attractive than other oxidation processes.

The important part of an anodic oxidation process is obviously the selected anode material[8]. Anode materials investigated include glassy carbon[9], Ti/RuO₂, Ti/Pt–Ir[10], MnO₂[11,12], Pt–carbon black[13,14], porous carbon felt[15], stainless steel[16], and reticulated vitreous carbon[17,18]. However, none of them have sufficient activity and at the same time stability. The anodes that were studied extensively are graphite, Pt, PbO₂, IrO₂, TiO₂, and diamond film [8].

The anodic oxidation of urea in solution containing chloride ions may be the result of direct electrode reaction, oxidation by chlorine produced during an anodic process, oxidation by chlorine adsorbed at the electrode or simultaneously by all of the above. The predominance of one of the mechanisms of electrochemical decomposition of urea and its products depend on factors such as anode material, type and concentration of the electrolyte which affects conductivity[2].

Voltammetric investigations into the process of anodic decomposition of urea using Ti/Pt, Ti/(Pt–Ir)₇₀:₃₀, Ti/RuO₂, Ti/(RuO₂–TiO₂)₄₀:₆₀, Ti/(RuO₂–TiO₂–IrO₂)₂₀:₆₀:₂₀, Ti/(Ta₂O₅–IrO₂)₇₀:₃₀ electrodes have been carried out. Two anodes namely (Ti/(Pt–Ir)₇₀:₃₀ and Ti/(Ta₂O₅–IrO₂)₇₀:₃₀) were found to be stable enough and indicated the required activity to produce non-toxic N₂ and CO₂ instead of nitrates and nitrates, the commonly reported electrochemical urea oxidation products[2].

Urea-rich wastewater has also been identified as a good source for hydrogen production in alkaline medium. The major constituent of human or animal waste on earth is urine, containing about 2–2.5 wt.% of urea suggesting the availability of a considerable amount of urea in municipal wastewater. Also, a large amount of wastewater with varying concentrations of urea is produced during the industrial synthesis of urea[19]. Urea electrolysis would be an efficient way for hydrogen production from urea-rich wastewater thus potentially using urine [19-23], the product of human/animal excretion as an energy source, as shown in Fig. 1. Urea is electrochemically oxidized at the anode producing N₂ and CO₂, whereas pure hydrogen is evolved at the cathode that can be collected as a valuable fuel and clean water is obtained as a by-product [19].

The anodic oxidation of urea with simultaneous evolution of hydrogen at the cathode can be represented by the following overall cell reaction:

\[
\text{CO (NH}_2\text{)}_2(aq) + \text{H}_2\text{O} \rightarrow \text{N}_2(g) + 3 \text{H}_2(aq) + \text{CO}_2(aq)
\]

(1)

The electrode reactions, whether in acidic or alkaline medium, would involve 6 electrons.

It is clear from the previous literature review that no attempt has been done to study the electrochemical removal of urea from wastewater on bench-scale level. Unlike phenol[20,21], aniline[22,23], and several other organic pollutants, urea electrochemical removal has not be subjected to extensive study beyond lab-scale level. The relatively low concentrations of urea in industrial wastewater necessitate the use of flow-through or flow-by electrodes to avoid mass-transfer limitations. These electrodes have been used in several applications[24-27] since they provide high mass-transfer coefficients and large electrode surface areas.

The three-dimensional porous electrodes offer particularly high values of the electro active area per unit reactor volume and give a moderate increase in mass transport coefficient. The result is a significantly increased performance from a given volume of reactor, compared to two-dimensional electrode materials.

Flow-by porous electrode work as flow-through porous electrode, but the difference between them is the electricity flow, which is perpendicular to that of electrolyte in case of flow-by and parallel in case of flow-through as shows in Fig.2.[28]

Trainham and Newman[28] published a comparison between flow-through and flow-by electrodes. They concluded that economically the flow-by electrode is superior than flow-through.

The flow-through reactor is impractical due to the extremely low flow rates required, its failure was identified as being due to having the current flow in the same direction as the fluid flow.[28].

Fedkiw[29] has made a similar comparison, but in different basis and reached the same conclusion that the flow-by electrodes is superior to flow-through electrodes.

The advantage of the porous electrode lies in the high rates of reaction, and consequently reaction is usually arranged to be under limiting-current conditions which
corresponds to the maximum rate of mass transfer \([28]\).

In this study, experiments were carried out using a bench-scale electrochemical cell incorporating flow-by porous graphite electrodes for decomposition of urea. The effects of current density, feed flow rate, composition of the electrolyte, and urea concentration in influent stream, on the removal rates, current efficiency and energy consumptions were investigated.

2-Experimental details

2.1 Materials

The used chemicals were urea with 99 % purity, sodium chloride with 99 % purity and sulfuric acid with 99 % purity. These chemicals were all of commercial grade.

The investigated solutions were prepared by dissolving urea and sodium chloride into distilled water to obtain the desired concentration, while sulfuric acid was added to obtain the desired pH.

2.2 Cell construction

A schematic of the experimental setup is shown in Fig. 3.

The porous electrodes were contained in a vertical Plexiglas cylinder of internal diameter of 20 cm, and height of 40 cm, with two end flanges made from PVC. The anode compartment was filed by graphite to a height of 27 cm.

A stainless steel screen (mesh 5) in the form of a cylinder with internal diameter of 10 cm was used as the cathode compartment. The anode compartment was the annular space between that stainless steel cylinder and the cell body.

Three stainless steel rods of 10 mm diameter and 50 mm length were used; two of them as current collectors in the anode compartment, while the third one in the cathode compartment.

Graphite powder with the screen analysis shown in Table 1 was poured into the anodic compartment, while graphite granules with 0.5 cm average particle diameter into the cathode compartment. The stainless steel cylinder was enclosed by a polyamide membrane to minimize any transfer of graphite between both compartments and to maintain electric separation between both compartments.

The feed entered through an opening at the bottom of the anode compartment, while the outlet flow and the gas vents were located at the upper flange of the anode and cathode compartments respectively.

A dosing pump of type Master Flex Cole-Palmer Instrument Company controlled the feed flow rate between 0.56 and 1.9 ml/s.

The cell was connected to laboratory DC power supply Model (GPR-1810 HD) that can supply current up to 10 A at potential up to 18 V. The potential and current were measured using digital multi-meters of type METEX M-3800.

2-3 Analysis

The characteristics of raw and treated water were determined by measuring the following parameters:
1- pH measured by using pH meter, model AD 1030 pH/mV
2- Urea concentration measured by using Spectrophotometer Genesys 105 UV-VIS \([30,31]\).

2-4 Methodology

Feed solution was fed to the anode compartment with controlled flow rate using the dosing pump. Triplicate effluent samples were collected in special bottles after 100, 120 and 140 minutes to ensure that steady state conditions were reached. The current and potential of the cell were recorded at the same sampling time. The average of the concentrations of the three samples was considered as the effluent concentration for each run. The temperature was adjusted using an electric heater with variable heat input and thermometer placed in the feed solution storage vessel.

2.5 Investigated parameters

The investigated parameters were: the apparent anodic cell current density \((J = 2 – 8 \text{ mA/cm}^2)\), influent flow rate \((Q = 0.56 – 1.6 \text{ ml/s})\), concentration of sodium chloride \((c_{\text{NaCl}} = 1000 – 10000 \text{ ppm})\) and initial concentration of synthetic urea solution \((c_i = 100 – 2500 \text{ ppm})\) where ppm equal to mg/l.

The results of the above measurements were used to calculate the removal rates, current efficiency, and energy consumption for electrochemical decomposition of urea:

The removal rate of urea was calculated from the following equation:

\[
R = Q (c_i - c_e) \times (3600) \quad (2)
\]

Where \(R\) is the removal rate of urea in g/h on the surface of graphite anode, \(Q\) is the flow rate of influent in ml/s, and \(c_i\) and \(c_e\) are the concentrations of urea in influent and effluent in ppm, respectively.

The theoretical current was calculated from the following equation:

\[
I_{th} = Q (c_i - c_e) (n) (965000)(M/1000,000) \quad (3)
\]

Where \(I_{th}\) is the theoretical current in A, \(M\) is the molar mass of urea\((M = 60.06 \text{ g/mol})\), \(n\) is the number of electrons exchanged during reaction \((1)\), \(n = 6\) and \(F\) is the Faraday constant \((\text{Ah/mol})\).

The current efficiency (C.E) of urea was calculated from the following equation:

\[
C.E = (I_{th} / I_{act}) \times 100 \quad (4)
\]

Where, \(I_{act}\) the actual current measured in A.

The energy consumption was calculated from the following equation:

\[
Z = (V * I_{act}) / R \quad (5)
\]

Where, \(Z\) is the energy consumption in kWh/kg of urea removed and \(V\) is the cell potential in volt.
3. Results and discussion

3.1 The influence of flow rate

Fig. 4 shows the variation of removal rate of urea with influent flow rate for different concentrations of urea. It is obvious that the removal rate of urea increases with the increase in influent flow rate. This trend agrees with results of Kirk and Sharifian [20] who used a lead dioxide packed bed anode with recirculating anolyte for electrochemical oxidation of phenol. Also this trend agrees with the results of De Sucre and Watkinson [32] who also used lead dioxide for anodic oxidation of phenol for wastewater treatment and operating both in batch and continuous modes.

At flow rates up to 1.6 ml/s, the removal rate of urea continuously increased due to the increase in mass-transfer coefficient. The change in the removal rate was negligible when the flow rate was increased from 1.6 to 1.9 ml/s. This is due to two opposing effects: the increase in mass-transfer coefficient due to the higher flow rates, and the decrease of residence time available for urea removal.

3.2 The influence of anodic current density

As shown in Fig. 5 and 6, increasing the current density, increased the rate of urea removal due to increase of the rate of urea decomposition on the anode, providing that the mass-transfer rate is high enough. However, above 5.6 mA/cm$^2$ the change in the removal rate was negligible as limiting current density is approached, where the interfacial concentration of urea on the graphite anode diminishes practically to zero.

As indicated in Fig. 7, an increase in anode current density from 2 to 8 mA/cm$^2$ at flow rate of 1.6 ml/s caused decrease in current efficiency from 82 to 30 % and from 59 to 17 % for initial urea concentration of 2500 and 800 ppm, respectively.

For the same conditions, the energy consumption increased from 11 to 71 kWh/kg, and from 16 to 104 kWh/kg as shown in Table 2.

3-3 The influence of initial urea concentration

An increase in initial urea concentration from 100 to 2500 ppm caused an increase in the removal rate as shows in Fig.8.

Table 3 shows, the current efficiency of the process increased as well from 13 to 52, while the energy consumption was reduced from 104 to 26 kWh/kg as shown in Table 3.

The results shown in Fig.8 are in agreement with Wojciech-Simka [2], who observed that the removal rate in anodic oxidation by Ti/(Ta$_2$O$_5$-IrO$_2$)$_{70:30}$ electrode and Ti/(Pt-Ir)$_{70:30}$ increased with an increase in initial urea concentration [3].

This observation was explained by Alkire [33], who observed that the removal rate of anodic oxidation using flow by porous electrode technique is mass-transfer controlled, when the flow rate increase at the same current density, the removal rate of urea increases.

3-4 The influence of sodium chloride concentration

The anodic oxidation of urea in solution containing chloride ions may be the result of direct electrode reaction, oxidation by chlorine produced during an anodic process, oxidation by chlorine adsorbed at the electrode or simultaneously by all of the above [35].

Table 4 shown, an increase in sodium chloride concentration led to an increase in the removal rate of urea. The increase in sodium chloride concentration improves the conductivity of solution which consequently decreases the potential drop (IR drop), and energy consumption. At the same time, the increase in sodium chloride concentration increased the amount of chlorine adsorbed on the electrode which might directly react with urea resulting in its oxidation. This is confirmed by the results shown in Table 4.

The current efficiency of the process increased as well from 27 to 85 %, and from 13 to 37 % for 2500 and 800 ppm, respectively.

As shown in Table 4 the energy consumption decreased from 60 to 18 kWh/kg and from 121 to 45 kWh/kg for 2500 and 800 ppm, respectively.

Fig. 1. Schematic representation of urea electrolysis unit and its applications.[14].
Table 1: Sieve Analysis of the Graphite powder

<table>
<thead>
<tr>
<th>Sieve no</th>
<th>Screen opening μm</th>
<th>Average particle diameter, Cm</th>
<th>Mass fraction retained</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>850</td>
<td>-</td>
<td>0.0623294</td>
</tr>
<tr>
<td>30</td>
<td>600</td>
<td>725 × 10^{-4}</td>
<td>0.1613734</td>
</tr>
<tr>
<td>45</td>
<td>355</td>
<td>477.5 × 10^{-4}</td>
<td>0.419561</td>
</tr>
<tr>
<td>60</td>
<td>250</td>
<td>302.5 × 10^{-4}</td>
<td>0.2739</td>
</tr>
<tr>
<td>100</td>
<td>150</td>
<td>200 × 10^{-4}</td>
<td>0.075073</td>
</tr>
<tr>
<td>200</td>
<td>75</td>
<td>112.5 × 10^{-4}</td>
<td>0.0052507</td>
</tr>
</tbody>
</table>

Fig. 2: Schematic diagram of a flow-by porous electrode.

Fig. 3: Schematic of Experimental setup (1- Cathode current collector, 2- Anode current collector, 3- Ammeter, 4- Voltmeter, 5- D.C power supply, 6- Plexiglas cylinder, 7- Stainless steel cylinder, 8- graphite, 9- urea solution tank, 10- gas vents, 11- treated water tank)

Fig. 4: Variation of removal rate of urea decomposed (R) with flow rate, at C_{urea}=5000 ppm, and current density J=5.6 ma/cm²
Table 2: Process energy consumption for anodic decomposition of urea

<table>
<thead>
<tr>
<th>C&lt;sub&gt;ini&lt;/sub&gt;, ppm</th>
<th>2500</th>
<th>800</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Current density</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>16</td>
<td>46.9</td>
</tr>
<tr>
<td>3</td>
<td>26</td>
<td>35</td>
<td>104.1</td>
</tr>
<tr>
<td>5.6</td>
<td>47.7</td>
<td>73</td>
<td>206.9</td>
</tr>
<tr>
<td>8</td>
<td>71</td>
<td>104</td>
<td>311.9</td>
</tr>
</tbody>
</table>
Table 3: Variation of current efficiency (C.E) and energy consumption (Z) of urea decomposition with different influent concentration at J = 3mA/cm².

<table>
<thead>
<tr>
<th>C_i [mg/l]</th>
<th>C.E [%]</th>
<th>Z [kWh/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>13</td>
<td>104.1</td>
</tr>
<tr>
<td>800</td>
<td>36</td>
<td>35</td>
</tr>
<tr>
<td>2500</td>
<td>52</td>
<td>26</td>
</tr>
</tbody>
</table>

Table 4: Variation of removal rate(R), C.E, and energy consumption(Z) of urea decomposition with different concentration of NaCl at flow rate 1.6 ml/s, and J = 3mA/cm².

<table>
<thead>
<tr>
<th>C NaCl, ppm</th>
<th>R, g/h</th>
<th>C.E [%]</th>
<th>Z [kWh/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
</tr>
<tr>
<td>1000</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>3000</td>
<td>0.58</td>
<td>0.58</td>
<td>0.58</td>
</tr>
<tr>
<td>5000</td>
<td>0.86</td>
<td>0.86</td>
<td>0.86</td>
</tr>
<tr>
<td>8000</td>
<td>1.09</td>
<td>1.09</td>
<td>1.09</td>
</tr>
<tr>
<td>10000</td>
<td>1.15</td>
<td>1.15</td>
<td>1.15</td>
</tr>
</tbody>
</table>

4. Conclusion

The relatively low concentrations of urea in industrial wastewater necessitate the use of flow-through or flow-by electrodes to avoid mass-transfer limitations. The advantage of the porous electrode lies in the high rates of reaction, and consequently reaction is usually arranged to be under limiting conditions.

In this study, it was proved that using flow-by porous graphite electrode for the treatment of wastewater contaminated with urea is an effective method. For it is recommended to use an influent flow rate of 1.6 ml/s at a current density 3 mA/cm². At these conditions the removal rates of urea was 0.4, and 0.58 g/h at current efficiencies of 40, and 50 and energy consumption of 35, and 26 kWh/kg for initial concentrations of 800 and 2500 ppm, respectively. The addition of sodium chloride improved the cell performance to a great extent. Thus, it is recommended to adjust the concentration of the NaCl in the influent steam to 8000 ppm. At this concentration of NaCl and at an influent concentration of urea of 2500 ppm, the cell efficiency is improved by a factor of 3, the energy consumption was also reduced by the same factor, while the removal rate of urea was improved from 0.35 to 1.09 g/h at an inflow of 1.6 ml/s and a current density of 3 mA/cm².

References
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