

# Oxidation of urea in human urine using flow-by porous graphite electrode

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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 oxidation of human urine was collected from a mosque during baths on urea were analyzed and found that the concentration ranges of urea between 50 to 100 ppm. The effect of anodic current density, and influent feed flow rate, on basic process indices, the removal rate of urea, and 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 human urine concentration of 100 ppm, the maximum current efficiency is 27, the maximum removal rate is 0.33 g/h, and minimum energy consumption is 196 kWh/kg.

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

## 1. Introduction

One of the effective measures to help solve the water shortage problem involves recycling of human urine for its use as flush water this is because while an adult passes approximately 1.5 L of urine per day, 10 times this amount water is used simply to flush this. Therefore, a large amount of water can be saved (approximately 20 L per person daily) if all the urine is recycled<sup>[1]</sup>.

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.

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<sup>[2]</sup>.

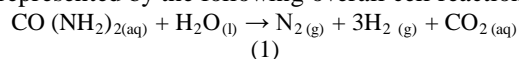
Urea was electrochemically treated in order to suppress the emission of the unpleasant odor due to ammonia, which is an end product of the hydrolysis of urea in urine

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<sup>[1]</sup>.

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<sup>[3-6]</sup>.

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<sup>[7]</sup>. Urea electrolysis would be an efficient way for hydrogen production from urea-rich wastewater thus potentially using urine<sup>[7-11]</sup>, the product of human/animal excretion as an energy source, as shown in Fig. 1. Urea is electrochemically oxidized at the anode producing N<sub>2</sub> and CO<sub>2</sub>, 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<sup>[7]</sup>.

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



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<sup>[12,13]</sup>, aniline<sup>[14,15]</sup>, and several other organic pollutants, urea electrochemical removal has not been 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<sup>[16-19]</sup> 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.1<sup>[20]</sup>.

Trainham and Newman<sup>[20]</sup> published a comparison between flow-through and flow-by electrodes. They concluded that economically the flow-by electrode is superior than flow-through.

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<sup>[20]</sup>.

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 Urine

Human urine was collected from a mosque during baths on urea were analyzed and found that the concentration ranges of urea between 50 to 100 ppm.

The investigated urine solutions were prepared by dissolving sodium chloride into human urine to obtain the desired concentration, while sulfuric acid

was added to obtain the desired pH and it was stored at 4 °C until use.

### 2.2 Cell construction

A schematic of the experimental setup is shown in Fig. 2.

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 filled 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<sup>[21, 22]</sup>.

### 2-4 Methodology

Human urine 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 ( $J = 1.8 - 7.8 \text{ mA/cm}^2$ ), and influent flow rate ( $Q = 0.56 - 1.9 \text{ ml/s}$ )

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

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

$$R = Q (c_i - c_o) (10^{-6}) (3600) \quad (2)$$

Where  $R$  is the removal rate of human urine in g/h on the surface of graphite anode,  $Q$  is the flow rate of influent in ml/s, and  $c_i$  and  $c_o$  are the concentrations of urea in influent and effluent in ppm, respectively.

The removal rate of human urea per unit volume of anodic compartment was calculated from the following equation;

$$R = [Q (c_i - c_o) (10^{-6}) (3600)] / A_{\text{anode}} \quad (3)$$

Where  $A_{\text{anode}}$  is area of anodic compartment in cubic meter.

The theoretical current was calculated from the following equation;

$$I_{th} = Q (c_i - c_o) (n) * (96500) (M/1000,000) \quad (4)$$

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 (Ah/mol).

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

$$C.E = (I_{th} / I_{act}) * 100 \quad (5)$$

Where,  $I_{act}$  the actual current measured in A.

The energy consumption was calculated from the following equation;

$$Z = (V * I_{act}) / R \quad (6)$$

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 effect of flow rate

Fig. 3 shows the variation of removal rate of urea with influent flow rate for different concentrations of human urine. It is obvious that the removal rate of urea increases with the increase in influent flow rate. This trend agrees with results of removal of urea from industrial wastewater using electrochemical oxidation<sup>[23]</sup> who used graphite anode for electrochemical oxidation of urea. Also this trend agrees with the results of De Sucre and Watkinson<sup>[24]</sup> 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 effect of anodic current density

As shown in Fig. 4 to 6, increasing the current density, increased the rate of urine removal due to increase of the rate of urea oxidized on the anode, providing that the mass-transfer rate is high enough. However, above  $5.6 \text{ mA/cm}^2$  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 1.78 to  $7.8 \text{ mA/cm}^2$  at flow rate of 1.6 ml/s, and best sodium chloride concentration  $8000 \text{ ppm}$ <sup>[23]</sup> caused decrease in current efficiency from 27 to 9 % and from 9 to 4 % for human urine concentration of 100 and 50 ppm, respectively.

For the same conditions, the energy consumption increased from 35 to 196 kWh/kg for human urine concentration of 100ppm.

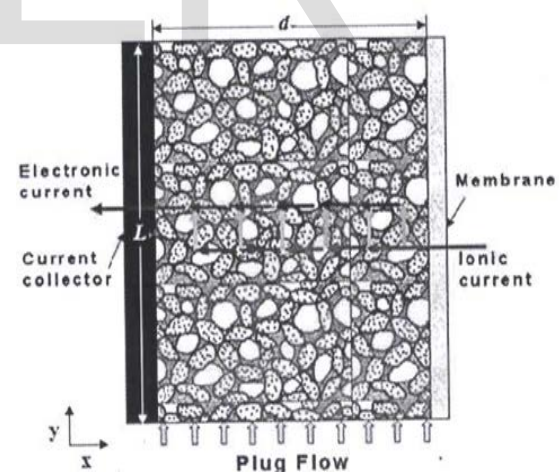
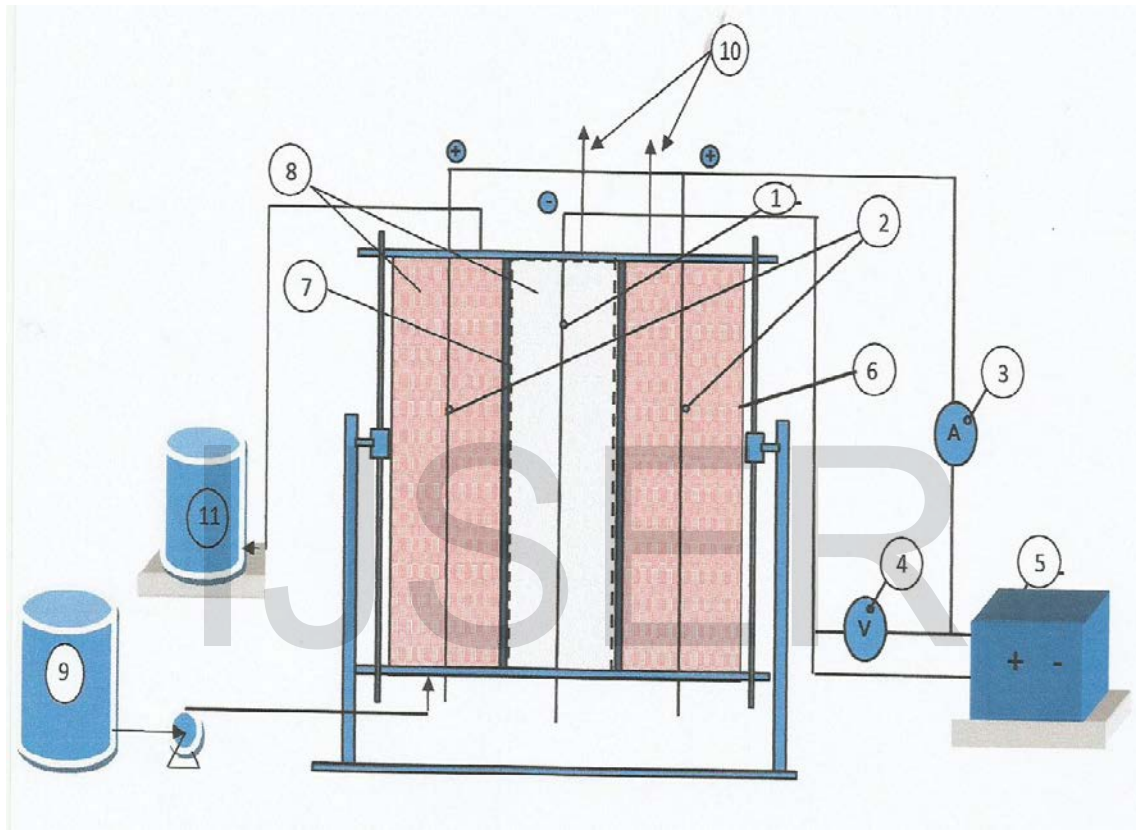


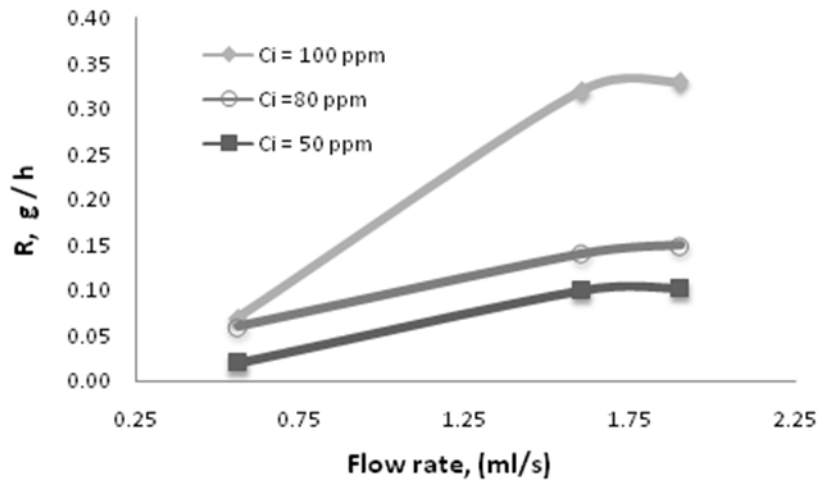
Fig.1 : Schematic diagram of a flow-by porous electrode.

**Table 1 : Sieve Analysis of the Graphite powder**

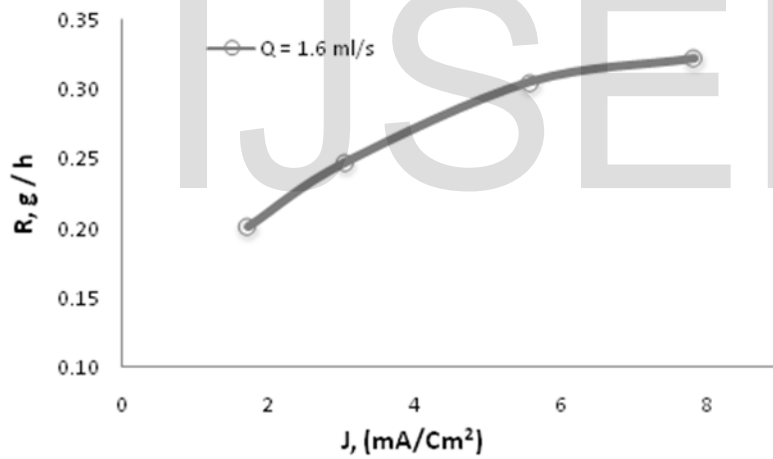
Sieve no	Screen opening $\mu\text{m}$	Average particle diameter, Cm	Mass fraction retained
20	850	-	0.0623294
30	600	$725 \times 10^{-4}$	0.1613734
45	355	$477.5 \times 10^{-4}$	0.419561
60	250	$302.5 \times 10^{-4}$	0.2739
100	150	$200 \times 10^{-4}$	0.075073
200	75	$112.5 \times 10^{-4}$	0.0052507



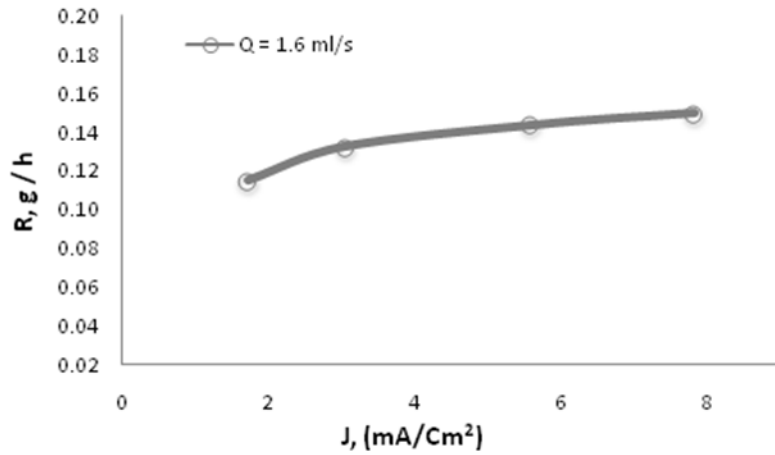
**Fig. 2: Schematic of Experimental setup ( 1- Cathode current collector , 2- Anode current collector , 3- Ammeter, 4- Voltmeter, 5- D.C power supply, 6- Plexiglas cylinder, 7-Stainless steel cylinder, 8- graphite, 9-urea solution tank,10- gas vents, 11- treated water tank)**



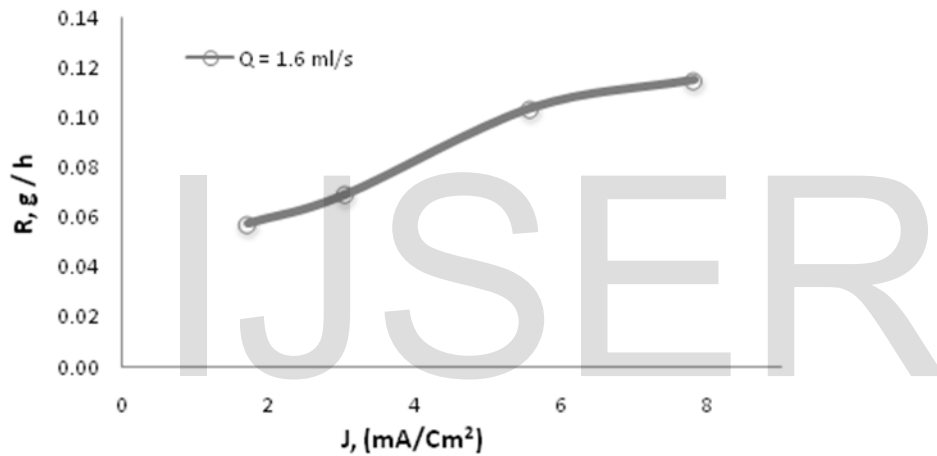
**Fig. 3 :** Variation of removal rate of urea decomposed ( $R$ ) with flow rate, at  $C_{NaCl} = 5000$  ppm, bed height = 27 cm, and current density  $J = 5.6$  mA/cm<sup>2</sup>



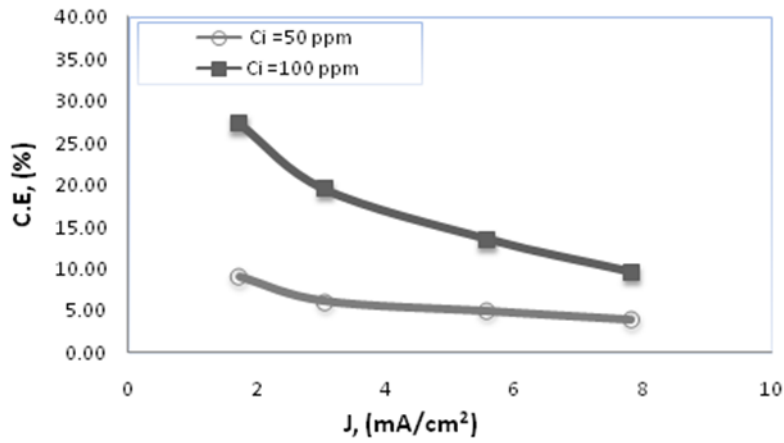
**Fig. 4 :** Variation of removal rate of urea decomposed, ( $R$ ) with current density, at  $C_i = 100$  ppm, and  $C_{NaCl} = 8000$  ppm .



**Fig. 5 :** Variation of removal rate of urea decomposed, ( $R$ ) with current density, at  $C_i = 80$  ppm, and  $C_{NaCl} = 8000$  ppm .



**Fig. 6 :** Variation of removal rate of urea decomposed, ( $R$ ) with current density, at  $C_i = 50$  ppm, and  $C_{NaCl} = 8000$  ppm .



**Fig. 7 :** Variation of current efficiency, with current density, at  $C_{NaCl} = 8000$  ppm and flow rate = 1.6 ml/s.

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#### 4. Conclusion

-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 human urine, for its use as flush water, is an effective method.

- For it is recommended to use an influent flow rate of 1.6 ml/s at a current density 5.6 mA/cm<sup>2</sup>, electrolyte concentration 8000 ppm, height of bed 27 cm, and pH 4. At these conditions the removal rates of urea was 0.33, and 0.1 g/h at current efficiencies of 14, and 6 % and energy consumption of 129, and 344 kWh/kg for initial concentrations of 100, and 50 ppm, respectively.

-The three of proposed cell can be introduced in the treatment of wastewater containing urea coming out of camps located far from civilian life or marble quarry.

-This cell can be used in the future in industrial effluent Treatment with small quantities of fertilizer factories during working day.

- This cell can be used in the future in dialyses process effluent Treatment before ditched in drainage systems.

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