Energy Conversion and Management 52 (2011) 2870–2875

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Mass transfer behavior of rotating square cylinder electrochemical reactor in relation to wastewater treatment

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ARTICLE INFO

Article history:
Received 6 May 2010
Received in revised form 27 February 2011
Accepted 7 April 2011
Available online 4 May 2011

Keywords:
Electrochemical reactor
Mass transfer
Rotating cylinder
Oxalic acid removal
Energy consumption

ABSTRACT

Rates of mass transfer at a rotating square cylinder were measured by an electrochemical technique which involved measuring the limiting current of the cathodic reduction of $K_3Fe(CN)_6$ in a large excess of NaOH solution. Variables studied were: cylinder rotation speed, physical properties of the solution and cylinder equivalent diameter. The data for the condition $1577 < Sc < 4117$, $1045 < Re < 67{,}803$ were found to fit the equation:

$$Sh = 2.1Sc^{0.33}Re^{0.45}$$

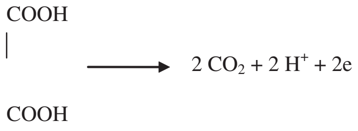
For a given set of conditions the rate of mass transfer at the square rotating cylinder was found to be higher than that at the traditional circular rotating cylinder by an amount ranging from 47% to 200% depending on Re. The use of the square rotating cylinder electrode in removing oxalic acid from wastewater by anodic oxidation on Pb/PbO anode was examined and found to be promising.

1. Introduction

In view of its high rate of mass transfer and uniform current and potential distribution the rotating cylinder electrochemical reactor has been used widely for removing heavy metals from industrial waste solutions and for electro-organic synthesis [1–3]. Since the pioneering work of Eisenberg et al. [4] on the mass transfer behavior of the rotating cylinder several attempts have been carried out to improve the performance of the rotating cylinder electrochemical reactor in conducting diffusion controlled reactions via:

1. Enhancing its rate of mass transfer by:
   (i) Roughening its surface [5–7].
   (ii) Using a wiper blade [8,9].
   (iii) Evolving gas simultaneous with the main reaction on the surface of the rotating cylinder [10].
   (iv) Superimposing axial flow on the flow induced by cylinder rotation in a continuous flow reactor [11–13].
2. Expanding its active area by using reticulated vitreous carbon rotating cylinder [14] and rotating cylinder of screen and expanded metal [15,16].
3. Decreasing its mechanical power consumption by drag reducing polymers [17–20]. Despite the great progress that has been made to improve the performance of the rotating cylinder electrochemical reactor we believe that there is still a room for further development. The aim of the present work is two fold namely:
   (i) To examine the performance of square rotating cylinder in conducting diffusion controlled reactions. Previous studies were limited to the circular rotating cylinders.
   (ii) To explore the possibility of using the rotating square cylinder electrochemical reactor in removing oxalic acid from waste water by anodic oxidation using Pb/PbO_2 anode.

Water pollution by oxalic acid is caused by industries such as the metal finishing industry, printing and textile industry [21,22]. Oxalic acid is also a metabolite of the catalytic oxidation of phenol and other aromatic substances [23]. Anodic oxidation of oxalic acid solutions leads to incineration of the acid according to the equation [23,24]



$$\begin{array}{l} COOH \\ | \\ COOH \end{array} \longrightarrow 2\,CO_2 + 2\,H^+ + 2e$$

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doi:10.1016/j.enconman.2011.04.001

Nomenclature

A	electrode area
A	constant
C_o	initial concentration
C	concentration at any time t
d_e	equivalent diameter of the square cylinder
d	diameter of the circular cylinder
D	diffusivity
E	cell voltage
F	Faraday's constant
I_m	maximum current used in oxalic acid anodic oxidation above which O_2 bubbles start to evolve
I_L	limiting current
K	mass transfer coefficient
m	amount of oxalic acid removed per hour
r	cylinder radius
t	time
V	linear speed of the rotating cylinder ($V = wr$)
Q	solution volume
R	cell resistance
Z	number of electrons involved in the reaction
Re	Reynolds number (Vd/γ)
Sh	Sherwood number (Kd/D)
Sc	Schmidt number (γ/D)
w	rotation speed (rpm/60)
γ	kinematic viscosity

Although previous voltametric kinetic studies on the anodic oxidation of oxalic acid [23,24] did not agree on a unified mechanism, these studies revealed that the rate of oxalic acid incineration as well as the mechanism depends largely on the nature of anode material. Mass transfer was found to play an important role in the kinetics of oxalic acid incineration when PbO_2 is used as anode [23]. PbO_2 is a good catalyst for the anodic oxidation of oxalic acid in view of its ability to promote the formation of OH radicals [23,25], in the mean time PbO_2 has a high oxygen over potential [25].

2. Experimental technique

The apparatus used in mass transfer study (Fig. 1) consisted of the cell and the electrical circuit. The cell consisted of 15 cm diameter cylindrical plexiglass container of 30 cm height. The cathode was a rotating square Ni plated copper cylinder connected to the shaft of a variable speed motor through a plastic sleeve. A stainless steel cylindrical screen lining the inner wall of the container acted as anode. Three cathodes of equivalent diameters 1.8, 2.9, and 3.7 cm were used. Rotation speed of the rotating cylinder which ranged from 0 to 1000 rpm was controlled with a variac and was measured by an optical tachometer. For the anodic oxidation of oxalic acid, a rotating lead anode of square cross section ($d_e = 3$ cm) was used, the cathode was a lead sheet lining the container wall.

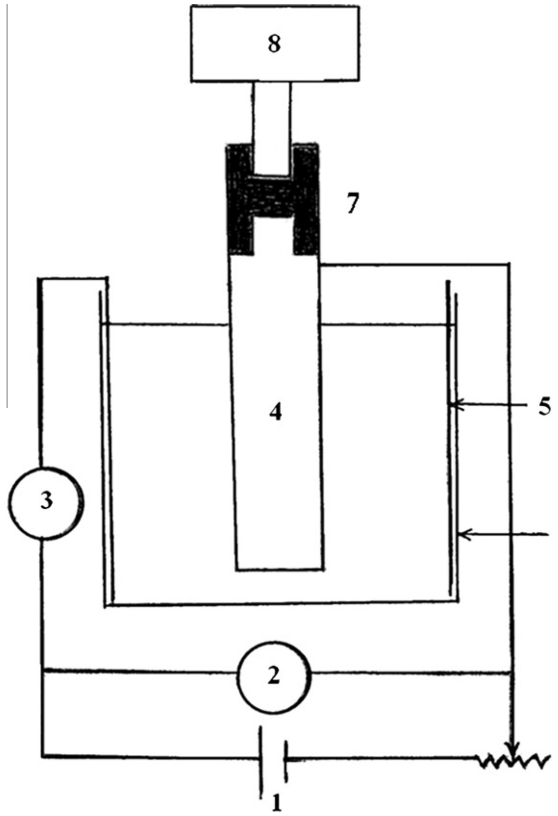

Fig. 1. Experimental apparatus (1) dc power supply; (2) voltmeter; (3) multirange ammeter; (4) rotating square cylinder cathode; (5) cylindrical stainless steel cathode; (6) plexiglass container; (7) plastic; (8) variable speed motor.

The electrical circuit consisted of 10 V dc power supply with a voltage regulator and a multirange ammeter connected in series with the cell, a voltmeter was connected in parallel with the cell to measure its voltage. Current was fed to the rotating cylinder via a metallic brush pressed against the upper part of rotating cylinder.

The mass transfer behavior of the rotating square cylinder was studied by measuring the limiting current of the cathodic reduction of $K_3Fe(CN)_6$ at the Ni plated copper cathode. The limiting current was determined from the current–potential curve which was plotted by increasing the current stepwise and measuring the corresponding cathode potential. In view of the large anode area compared to the cathode area and the high ratio between ferrocyanide and ferricyanide concentration used, the anode was taken as a reference electrode against which the cathode potential was measured [26]. This obviated the need to use external reference electrode and a Luggin tube which may disturb the hydrodynamic conditions in the cell.

Before each run 3 l of the solution were placed in the cell, three solutions of different composition were used, in all cases 0.01 M $K_3Fe(CN)_6$ + 0.1 M $K_4Fe(CN)_6$ were used but with three different NaOH concentrations namely; 1 M, 2 M, and 3 M. All solutions were prepared using distilled water and AR grade chemicals. The bottom of the rotating cathode was isolated with epoxy resin. Temperature was 25 ± 1 °C.

The rate of oxalic acid incineration by galvanostatic anodic oxidation at a rotating square cylinder of Pb/PO_2 was studied using 1 M H_2SO_4 as a supporting electrolyte and four different oxalic acid concentration namely 0.3, 0.2, 0.1, and 0.05 M. Electrolysis was conducted at the maximum current (I_m) above which O_2 bubbles start to evolve. The rate of oxalic acid oxidation was followed by withdrawing 5 cm^3 every 5 min for analysis. Oxalic acid analysis was carried out by titration against standard permanganate solution [27].

3. Results and discussion

3.1. Mass transfer at square rotating cylinder

Fig. 2 shows typical polarization curves with a well defined limiting current plateau obtained for the cathodic reduction of