Kinetics for electro-oxidation of organic pollutants by using a packed-bed electrode reactor (PBER)

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HIGHLIGHTS

- A novel [3]SRT was proposed to describe electro-oxidation of organic pollutants.
- Mixed-phase controlled (MPC) regime is a distinct characteristic of the bed electrode.
- Existence of the MPC is for difference of current density on metallic and particulate anode.
- Current utilization ratio (γ) is used to describe overall kinetics of anode materials.
- The [3]SRT can accurately predict electro-treatment of synthetic and real industrial wastewaters.

GRAPHICAL ABSTRACT
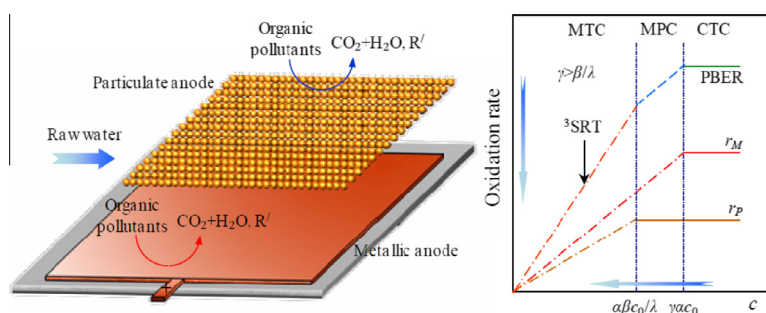
ABSTRACT

According to the intrinsic kinetics of electro-oxidation, a novel three-stage reaction theory ([3]SRT) involved charge transfer controlled (CTC), mixed-phase controlled (MPC) and mass transport controlled (MTC) regimes is presented to describe the oxidation of organic pollutants by using a packed-bed electrode reactor (PBER). The proposed [3]SRT could be universally used for overall oxidation due to the introduction of a parameter, current utilization ratio of γ ($\sim$1.0) related to anode materials. The existence of MPC regime is due to the difference of the applied current density between metallic anode and bipolar activated carbon (AC) particulate anode caused by the difference of the electrode area of the two kinds of anodes. The proposed theory was employed for prediction of chemical oxygen demand (COD) during treatment of synthetic phenolic wastewater, thiophene-2,5-dicarboxylic acid manufacturing wastewater and pyridine wastewater by using IrO_2 doped tantalum oxide (IrO_2-Ta_2O_5/Ti) anode. The regression analysis and *F*-test results illustrate the [3]SRT satisfactorily matches the experimental data obtained at different operation conditions such as current density, initial COD values and flow rate. These results confirm the proposed [3]SRT could effectively predict the change of concentration of organic pollutants during electro-oxidation by using a PBER.

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1. Introduction

Electrochemical processes are frequently used in effective treatment of industrial wastewaters and show dominant superiority to others advanced oxidation processes [1–3]. Therefore, aiming to predict the change of concentration of organic pollutants, modeling the electro-oxidation becomes a key issue in this field. Till to now, first-order kinetics has still been employed to describe the concentration evolution of organic pollutants [4,5], however, the empirical model could only provide a post-experiment regression of experimental results. Recently, a subsection model composed of the charge transfer controlled (CTC) and mass transport controlled (MTC) regimes has been proposed by Comninellis and his co-workers based on the assumption of complete oxidation of organic compounds and the theory was successfully achieved on boron-doped diamond (BDD) anode [6,7]. As regards others anodes, such as PbO_2, SnO_2, IrO_2 and carbon, especially for packed-bed electrode reactor (PBER), properly mathematic model barely exists; hence, proposal of suitable kinetics would be very useful for the industrial-scale application of this technology.

In this paper, a three-stage reaction theory (^{3}SRT) involved CTC, mixed-phase controlled (MPC) and MTC regimes was presented for accurate prediction of concentration of organic pollutants during electro-oxidation by using a carbon based PBER. The main differences between the ^{3}SRT and previous model are proposal of the MPC regime and introduction of the current utilization ratios of γ (~ 1.0) and β (~ 1.0) related to anode materials and surface characters of activated carbon (AC) particles, respectively. Moreover, a theoretical method for determination of expansion area of the particulate anode A_P by bipolar AC particles was provided. Further, the presented theory was checked by electro-oxidation of phenol and organic pollutants in thiophene-2,5-dicarboxylic acid manufacturing wastewater (TDAW) and pyridine wastewater by using IrO_2 doped tantalum oxide (IrO_2-Ta_2O_5/Ti) anode in a lab-scale PBER.

2. Experimental

2.1. Chemicals and materials

All reagents used for analysis were obtained in extra pure condition. The phenol (in 99.5% pure) was used for the preparation of synthetic wastewater. The AC used in the experiments has a specific surface area of 562 m^2/g and an average particle diameter of 5.0 mm obtained through screening separation, which was washed many times with distilled water to eliminate the fines and ashes, then oven-dried at 105 °C for 48 h to a constant weight prior to each experiment.

2.2. Experimental set-up

The treatment process was composed of eight cells with dimension size of $100 \times 50 \times 150$ mm and they were made of polymethyl methacrylate plastics. Each reactor was equipped with a pair of IrO_2-Ta_2O_5/Ti and Ti plates (100×100 mm) employed as anode and cathode, respectively, and approximately 350 g AC was packed between electrode gap up to a height of about 100 mm. A micropore plate was installed at the bottom of the cell to support the weight of AC and electrodes, and employed as solution distributor. A wriggle pump was used to pump the solutions into the reactor and the effective volume of each cell was about 0.21 L. The direct power supply (model: KZD300/12) having capacity of 0–300 A/0–12 V was purchased from Dazhong Company, China. The detailed information of the process was reported elsewhere [8,9] and the following experiments were carried out in a continuous flow mode at room temperature.

2.3. Wastewater quality

Synthetic phenolic wastewater (pH 6.5, 600 mg/L phenol, 3% (w/w) Na_2SO_4) was prepared by distilled water and the chemical oxygen demand (COD) values were ranged from 1321 mg/L to 1420 mg/L. The TDAW and pyridine wastewater with saline content (NaCl) of 8.6% and 10.9% (w/w), respectively, were filtered by a quartz sand based filtration in order to avoid blockage of AC bed by suspended solid in the raw solutions. After effective pretreatment, the average COD values of the two real industrial wastewaters were 5666 mg/L and 16,000 mg/L, respectively.

2.4. Analytical methods

The COD content was determined by the standard methods [10]. Prior to measurement, all the samples were filtered to removal any trace of AC powders and immediately analyzed to avoid further reaction. The values of β and γ could be calculated by COD reduction trends in CTC regime at the absence and presence of AC with description of Eqs. (1) and (2), respectively

$$\gamma = \frac{nFQ[c_0 - c(t)]}{z_0 \int_0^{y_0} i_M dy} \tag{1}$$

$$\beta = \frac{nFQ[c_0 - c(t)]}{z_0 \int_0^{y_0} i_M dy} - \gamma \tag{2}$$

where n is the electrons transferred during oxidation, F the Faraday's constant, Q the flow rate; c_0 and $c(t)$ denote the concentration of reactants initially and at reaction time t, z_0 and y_0 refer the width and height of the metallic anode, y is the flow through distance at $c(t)$, and i_M is the applied current density calculated by the geometrical area of metallic anode A_M.

The expansion area of AC bipolar anode A_P can be calculated by following equation:

$$A_P = V_{\text{eff}} a_{\text{sp}} - A_M \tag{3}$$

where V_{eff} and a_{sp} are the effective volume and specific area of the PBER. The value of the parameter a_{sp} could be achieved using the mathematical method as following.

The current density in solution ($i_s(x)$) perpendicular to the electrodes varies with its local one ($j_s(x)$) in x direction

$$\frac{di_s(x)}{dx} = -a_{\text{sp}} j_s(x) \tag{4}$$

In terms of CTC regime, $j_s(x)$ is equivalent to i_M values, i.e.

$$j_s(x) = i_M \tag{5}$$

Combination of Eqs. (4) and (5) gives

$$\frac{d^2 \varphi_s(x)}{dx^2} = -\frac{a_{\text{sp}}}{\sigma_s} i_M \tag{6}$$

where $\varphi_s(x)$ and σ_s are the potential in solution and solution conductivity, respectively. Eq. (6) is completed by introduction of the boundary conditions:

- At the inner boundary of the structure $x = 0$, the potential is constant and $\varphi_s(0) = 0$ if the cathode potential is employed as feed one.
- The outer boundary ($x = x_0$) is an insulator and $\frac{d\varphi_s(x)}{dx} = 0$, that is no current flow through it.

Here, the dimensionless inter-electrode distance (X) is defined

$$X = \frac{x}{x_0} \tag{7}$$