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Short communication

Linear control of electrochemical tubular reactor system—Removal of Cr(VI) from wastewaters

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ABSTRACT

An electrochemical tubular reactor system, which is used to remove the hexavalent chromium Cr(VI) from wastewaters, is presented. Under specific modeling and operating constraints, the axial dispersion reactor is described by the coupled nonlinear partial differential equations (PDEs) under Danckwerts boundary conditions. Through the composite finite difference combination, the lumped differential-algebraic equations (DAEs) turn out to be a two-input/two-output system. The overall system stability analysis is investigated via the Lyapunov's first method. According to the prescribed control configuration, the closed-loop simulation shows that a multi-loop PID control scheme can ensure the outlet concentration of Cr(VI) less than 0.5 mg/L in wastewaters.

1. Introduction

Hexvalent chromium Cr(VI) is one of the most worrying pollutants from the electroplating plants. Cr(VI) is generally considered 1000 times more toxic than Cr(III), so it is highly dangerous to human health. Since wastewaters with Cr(VI) are sources of groundwater contamination, this hazardous material should be limited to its acceptable concentration level for wastewater disposal. There are a number of technologies (Eckenfelder, 2000) to remove Cr(VI) from wastewaters, *e.g.* evaporation, ion exchange and ferrous sulfate. However, these methods usually produce a large amount of sludge to increase the additional cost of treatment and handling of the final disposal. Regarding the electrochemical treatment of chemicals in wastewaters, Rodríguez *et al.* (2003) developed the kinetic model for the Cr(VI) removal in an electrochemical continuous stirred reactor, Park *et al.* (2008) showed that the removal rate of Cr(VI) was affected by the variation of pH value or temperature, Rodríguez *et al.* (2009) studied a electrochemical flow reactor-in-series to calibrate the Cr(VI) removal model at different current density conditions, and Puebla *et al.* (2009) used an observed-based control to regulate the outlet concentration of Cr(VI) of the pilot-plant electrochemical reactor. On the other hand, Martínez and Rodríguez (2007) showed that a pilot-scale tubular reactor can effectively reduce the Cr(VI) concentration in wastewaters by exploiting the specific electrolysis design with a spiral wire of the anode and an inner straight tube of the cathode.

Generally, the tubular reactor is usually the typical distributed parameter system described by the partial differential equations (PDEs). Vande Wouwer *et al.* (2004) proposed one representative algorithm to solve a class of PDE systems using the Matlab toolbox. Lee *et al.* (2006) introduced the modeling and control of activated sludge processes which were solved by specific numerical methods. The stability properties of distributed parameter systems were validated on tubular reactor models (Winkin *et al.*, 2000; Aksikas *et al.*, 2007). Moreover, Chistofides (2001) introduced the new nonlinear feedback controllers of distributed parameter systems that take into account both the distributed and nonlinearities. The electrochemical reactor may be an adequate device to remove Cr(VI) from wastewaters. Recently, Aguilar *et al.* (2005) pointed out that the nonlinear control design with an online observer was used to regulate the output of the reactor and exactly meet environmental constraints.

This work presents the dynamic modeling and control design of a non-isothermal electrochemical tubular reactor. Since the dynamic system is described by coupled nonlinear parabolic PDEs, a lumped differential-algebraic equation (DAE) model via the space discretization is treated as a reduced-order two-input/two-output system. Through the conventional Lyapunov stability analysis, the open-loop stability property is guaranteed. Within the multi-loop PID control framework, closed-loop simulations shows that the system temperature can be regulated at the desired setpoint as well as the concentration of Cr(VI) can be effectively reduced by manipulating two specified variables of the electrochemical tubular system.

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Nomenclature

Cr(VI)	hexavalent chromium concentration in the reactor (mg/L)
Cr_0	the inlet concentration of hexavalent chromium (mg/L)
D	dispersion coefficient (cm^2/min)
c_{pm}	heat capacity of fluid (kcal/mol K)
I	current density (A/m^2)
k_1, k_2	rate constants
L	length of reactor (m)
T	reactor temperature (K)
T_0	inlet temperature of wastewater (K)
t_h	hydraulic residence time (min)
u	flow velocity (cm/min)
ρ_m	fluid density (kg/dm^3)
ΔH	heat of reaction (kcal/mol)

2. Electrochemical tubular reactor

Referring the experimental-scale apparatus for Cr(VI) removal from wastewaters (Martínez and Rodríguez, 2007), the structure of the electrochemical tubular reactor is depicted in Fig. 1, which should follow the specific operating conditions of Taiwan environmental laws for wastewater disposal, *i.e.* the outlet Cr(VI) concentration should be less than the 0.5 mg/L in wastewaters (Wang and Tsai, 2004). Assumed that the maximum 4 cm^3/min wastewater with Cr(VI) concentration around 1000 mg/L can be treated, in our configuration the inner tube wall and a central polished carbon steel rod with about 110 cm are served as the cathode. The cathode area is about 0.203 m^2. The long spiral carbon steel wire with about 6 m is treated as the anode. The anode area is about 0.1 m^2. Notably, the reactor body has one sampling port, the direct current control device provides a range of current density of 0–20 A/m^2 to the electrodes, and the influent wastewater blended with the addition of sulfuric acid is kept at constant pH values. In our approach, the inlet flow rate is manipulated to regulate the concentration of Cr(VI) at the assigned sampling port with aid of devices of composition analyzer/transmitter (AT), composition controller (AC) and control valve, and the current density on the electrodes is adjusted to affect the reactor temperature at the same sampling port with aid of devices of the temperature sensor/transmitter (TT) and the direct current power supply as regulator. Based on the presented control configuration in Fig. 1, the dynamic modeling, simulation, operation, and control are explored in this article *a priori*.

2.1. Partial differential equations (PDEs) system

The Cr(VI) reduction rate (r_{Cr}) is assumed as a reaction of shifting order (Rodríguez *et al.*, 2009; Puebla *et al.*, 2009), so the rate equation is described by

$$r_{Cr} = \frac{k_1(I)\mathrm{Cr(VI)}}{1 + k_2(I)\mathrm{Cr(VI)}} = \frac{0.7483\exp(-0.001 \times I)\mathrm{Cr(VI)}}{1 + 0.1772\exp(-0.003 \times I)\mathrm{Cr(VI)}} \quad (1)$$

where k_1 and k_2 are rate constants. Notably, Cr(VI) reduction depends on the current density. If the system is considered as a plug flow reactor with the effect of axial dispersion, then the mass balance for the Cr(VI) concentration in the fluid phase is given by

$$t_h\frac{\partial \mathrm{Cr(VI)}(z,t)}{\partial t} = \frac{D}{uL}\frac{\partial^2 \mathrm{Cr(VI)}(z,t)}{\partial z^2} - \frac{\partial \mathrm{Cr(VI)}(z,t)}{\partial z} - t_h\frac{k_1(I)\mathrm{Cr(VI)}(z,t)}{1 + k_2(I)\mathrm{Cr(VI)}(z,t)} \quad (2)$$

with initial condition

$$\mathrm{Cr(VI)}(z,0) = \mathrm{Cr_{ss}(VI)}(z) \quad (3)$$

and Danckwerts boundary conditions (Danckwerts, 1953) are

$$\mathrm{Cr(VI)}(0,t) - \frac{D}{uL}\frac{\partial \mathrm{Cr(VI)}}{\partial z}\bigg|_{z=0} - \mathrm{Cr}_0(t) = 0, \quad \frac{\partial \mathrm{Cr(VI)}}{\partial z}\bigg|_{z=1} = 0 \quad (4)$$

where t_h is hydraulic residence time, D is the dispersion coefficient, u is flow velocity, L is the length of the reactor. Notably, t_h is assumed as constant since the liquid flows inside a spiral pathway. Cr_0 is the inlet concentration of Cr(VI), and Cr_{ss}(VI) is the steady-state value of Cr(VI). According to Danckwerts boundary conditions, the outlet concentration of Cr(VI) should be minimized and the electrochemical reaction is not considered at the outlet.

The wastewater is less conductive, but the current passing over the electrodes may warm up the fluid. A little amount of water is dissociated into hydrogen and oxygen gases, so the thermodynamic equilibrium is not considered in this process. If heat losses are negligible and densities and heat capacity of fluid are constant, then the energy balance for this reactor is described by

$$t_h\frac{\partial T(z,t)}{\partial t} = \frac{D}{uL}\frac{\partial^2 T(z,t)}{\partial z^2} + \frac{\partial T(z,t)}{\partial z} + t_h\frac{(-\Delta H)}{\rho_m c_{pm}} \times \frac{k_1(I)\mathrm{Cr(VI)}(z,t)}{1 + k_2(I)\mathrm{Cr(VI)}(z,t)} \quad (5)$$

with initial condition

$$T(z,0) = T_{ss}(z) \quad (6)$$

and the Danckwerts boundary conditions are

$$T(0,t) - \frac{D}{uL}\frac{\partial T}{\partial z}\bigg|_{z=0} - T_0(t) = 0, \quad \frac{\partial T}{\partial z}\bigg|_{z=1} = 0 \quad (7)$$

where T_0 is the inlet temperature of wastewater, and T_{ss} (z) is the steady-state value of reactor temperature. Similarly, the Danckwerts boundary conditions show that the outlet reactor temperature should be maximized and the reaction heat is omitted at the outlet.

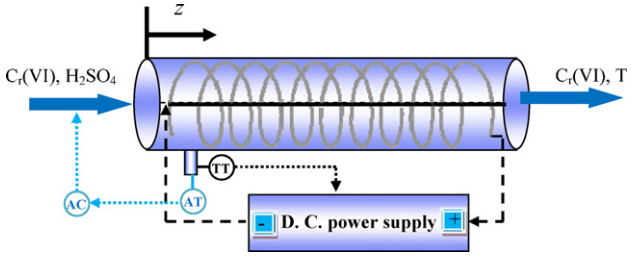

Fig. 1. Cr(VI) removal system and its control implementation.

2.2. Lumped differential-algebraic-equation (DAE) system

In general, one of Matlab PDE solvers, pdepe, was used to solve initial-boundary value problems for systems of parabolic PDEs in the one space variable x and time t. The pdepe solver can convert the PDEs to ODEs using a second-order accurate spatial discretization based on a fixed set of user-specified nodes. Using this Matlab PDE solver, the finite difference technique is usually chosen as the