A mathematical model to predict the electrode potential profile inside a polyaniline-modified reticulate vitreous carbon electrode operating in the potentiostatic reduction of Cr(VI)

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ABSTRACT

Hexavalent chromium compounds are very toxic and commonly found in the effluents of several industrial processes. Its reduction to the trivalent state is necessary in order to facilitate its removal from aqueous effluents using chemical precipitation or adsorption. The electrochemical process using conducting polymers deposited on reticulated vitreous carbon (RVC) has been considered as a promising alternative to chemical methods. In this work a polyaniline-modified RVC electrode was used in a potentiostatic process to reduce Cr(VI) to Cr(III). Two mathematical models considering a PFR and CSTR reactors were used to determine the mass transfer coefficients from the experimental concentration–time curves. The potential distribution was also measured and compared with the values obtained from a mathematical model. The effective conductivity and tortuosity were also determined. Approximately 80% of the Cr(VI) was reduced to its trivalent form during fifty minutes of electrolysis, giving an overall current efficiency and energy consumption of 0.71 and 4.4 kWh kg^{-1}, respectively. The high correlation coefficients ($R^2 > 0.999$) obtained using PFR and CSTR models confirmed that the assumption of limiting current (I_L) kinetics can be effectively used to describe the potentiostatic reduction. Additionally, k_m determined by CSTR, PFR and I_L equations had practically the same value. However, the tortuosity must be considered in the mathematical model to accordingly predict the potential profile.

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1. Introduction

Effluents containing hexavalent chromium are generated by a large variety of industries, such as metal finishing, inks, electronics, and metallurgy, among others. Due to its toxic effects, such as mutagenicity, genotoxicity, and carcinogenicity, the Cr(VI) concentration in industrial effluents is strictly controlled [1].

The oxidation states of chromium commonly found in nature are III and VI. However, while the Cr(VI) is very mobile in nature, Cr(III) can be easily precipitated or adsorbed over a variety of organic and inorganic substrates in pH close to the neutral. Thus, the reduction of chromium from hexavalent to trivalent state serves to immobilize it, to facilitate the next step of the effluent treatment and to reduce its toxicity, since compounds of Cr(III) have been reported as being 10–100 times less toxic than Cr(VI) compounds [2].

The conventional process used nowadays to reduce Cr(VI) is based on chemicals such as iron (II) chloride or sodium bisulfate. These chemicals are irreversibly consumed in a chemical reaction and cannot be recovered for reuse. Additionally, in some cases they contribute to increase the volume of sludge generated in the chemical precipitation of Cr(III), necessary to remove all chromium from the liquid phase.

Considering all the drawbacks earlier discussed, it has been recognized, either from the economical or environmental point of view, that the development of new technologies to improve or substitute the conventional treatment process of effluents containing Cr(VI) is very desirable. Some alternatives have been studied, such as the development of new adsorbents for Cr(VI), photochemical, and electrochemical processes.

Among the electrochemical processes, the first trial was the direct electroreduction of Cr(VI) to Cr(III); however, due to the low current efficiency, this process was not economically feasible. In order to overcome this problem, in a second trial the redox couple Fe$^{2+/3+}$ was used to intermediate the reaction and indirectly reduce the Cr(VI); this process was very effective, but an additional step was necessary in order to remove the iron ions from the effluent [3].

Processes using conducting polymer films deposited on large surface area substrates could eliminate the additional stage of separation, as in the case of Fe$^{2+/3+}$ mediator. Among the several applications of conducting polymers, their use for reduction of Cr(VI) started with Wei et al. [2], using polypyrrole. This process

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Nomenclature

A_e	specific surface area
C	concentration of reactant
C_0	initial concentration of reactant
D	diffusion coefficient
E	electrode potential
E_0	applied electrode potential
F	Faraday constant
F (Eq. (26))	formation factor
HER	hydrogen evolution reaction
i	current density
i^*	charge transfer flux (electrochemical kinetics)
I	current
ICE	instantaneous current efficiency
IEC	instantaneous energy consumption
k_m	mass transfer coefficient
M	molar mass
ppi	pores per inch
PANI	polyaniline
R	mass production rate per volume unit
RVC	reticulated vitreous carbon
t	time
T	tortuosity
v	flow velocity
V	electrolyte volume
x	electrode thickness coordinate
z	electrode height coordinate
Z	electrode height

Greek letters

ε	porosity
κ	conductivity
μ	ion mobility
σ	phase conductivity
τ	residence time
φ	electric potential

Subscripts

eff	effective
k	chemical specie
l	liquid phase
lim	limiting current
R	reactor
s	solid phase
T	tank
TE	tank entrance
TS	tank exit
α	phase

Fig. 1. Schematic representation of the experimental system: (1) electrolyte reservoir; (2) centrifugal pump; (3) flowmeter; (4) diaphragm valve; (5) voltmeter; (6) electrochemical reactor; (7) potential measurement device; (8) potentiostat; (9) computer for potentiostat and spectrophotometer control; (10) by-pass valve; (11) UV–vis spectrophotometer; (12) peristaltic pump.

dation product [5]. Due to this problem, the modified-polyaniline RVC electrode was tested in a continuous Cr(VI) reduction process applying a continuous cathodic potential in order to avoid the existence of the very anodic potentials responsible for the polymer degradation observed under *occ* [6]. This new method was very efficient and avoided the polymer degradation [7,8]. In this work we studied the potential distribution inside a three-dimensional electrode of polyaniline-modified reticulated vitreous carbon electrode (RVC/PANI). A mathematical model was developed and used to describe the potential distribution during the potentiostatic reduction of Cr(VI). Assuming the limiting current kinetics, the mass transfer coefficient for different flow velocities was also determined.

2. Experimental

The polyaniline was chosen to be used in this work since it can be easily prepared in an aqueous solution, moreover, its monomer is very inexpensive.

The experiments of Cr(VI) reduction were performed using the system and electrochemical reactor shown in Figs. 1 and 2, respec-

is based on the spontaneous electron transfer from polymer to Cr(VI) present in diluted aqueous solutions. The process suggested by these authors starts depositing the conducting polymer on a conducting substrate which is emerged in a solution containing Cr(VI), under open circuit condition. The polymer oxides and promotes the Cr(VI) reduction to Cr(III). After complete polymer oxidation, it can be reduced again to its reduced state by applying a cathodic potential, thus becoming able to be used in a new Cr(VI) reduction cycle. Despite the success obtained for Cr(VI) reduction, polymer degradation was observed after some cycles. According to Malinauskas and Holze [4], the contact between the polymer film (in this case, they used polyaniline) and the Cr(VI) solution under *occ* has the same effect of keeping it under very anodic potentials, in which polymer hydrolysis produces *p*-benzoquinone, as the main degra-
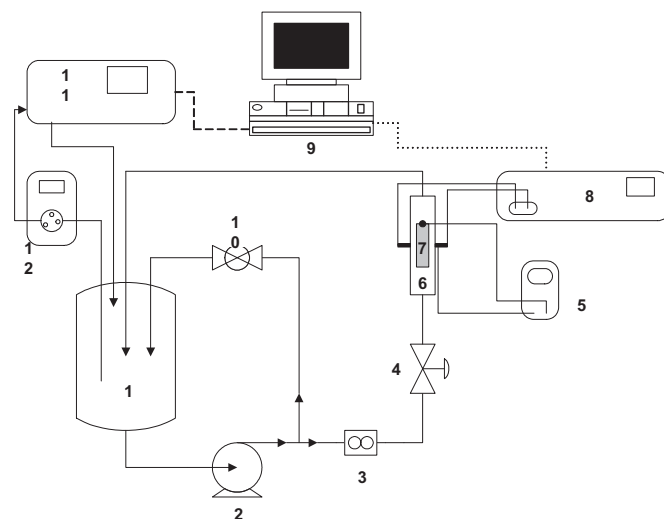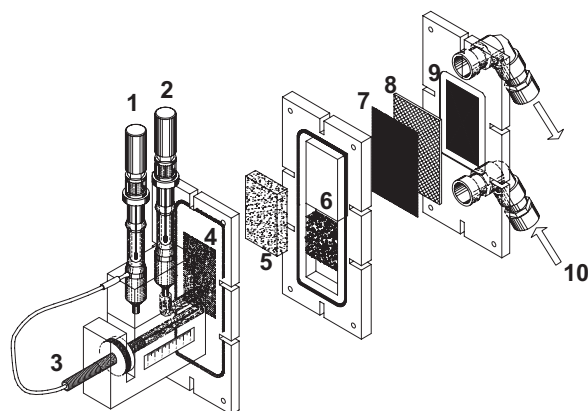

Fig. 2. Electrochemical reactor: (1) Ag/AgCl reference electrodes; (2) fixed Luggin capillary; (3) mobile Luggin capillary; (4) current feeder (stainless steel); (5) RVC; (6) flow distributor; (7) polyamide fabric; (8) polyethylene mesh; (9) counter electrode (Ti/Ti$_{0.7}$Ru$_{0.3}$O$_2$); and (10) electrolyte flow.