Available online at www.sciencedirect.com

ScienceDirect

Journal of Hazardous Materials 150 (2008) 46–52

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Modelling Cr(VI) removal by a combined carbon-activated sludge system

A. Micaela Ferro Orozco [a], Edgardo M. Contreras [a,*], Noemí E. Zaritzky [a,b]

[a] *Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA), CONICET, Fac. de Cs. Exactas, UNLP. 47 y 116 (B1900AJJ), La Plata, Argentina*

[b] *Fac. de Ingeniería, UNLP. 47 y 1 (B1900AJJ), La Plata, Argentina*

Received 1 November 2006; received in revised form 11 April 2007; accepted 17 April 2007
Available online 20 April 2007

Abstract

The combined carbon-activated sludge process has been proposed as an alternative to protect the biomass against toxic substances in wastewaters; however, the information about the effect of powdered-activated carbon (PAC) addition in activated sludge reactors for the treatment of wastewaters containing Cr(VI) is limited. The objectives of the present study were: (a) to evaluate the removal of hexavalent chromium by (i) activated sludge microorganisms in aerobic batch reactors, (ii) powdered-activated carbon, and (iii) the combined action of powdered-activated carbon and biomass; (b) to propose mathematical models that interpret the experimental results.

Different Cr(VI) removal systems were tested: (S1) biomass (activated sludge), (S2) PAC, and (S3) the combined activated carbon–biomass system. A Monod-based mathematical model was used to describe the kinetics of Cr(VI) removal in the system S1. A first-order kinetics with respect to Cr(VI) and PAC respectively, was proposed to model the removal of Cr(VI) in the system S2. Cr(VI) removal in the combined carbon–biomass system (S3) was faster than both Cr(VI) removal using PAC or activated sludge individually. Results showed that the removal of Cr(VI) using the activated carbon–biomass system (S3) was adequately described by combining the kinetic equations proposed for the systems S1 and S2.

Keywords: Chromium removal; Activated sludge; Activated carbon; Combined activated carbon–biomass system

1. Introduction

Heavy metal residues in contaminated habitats may accumulate in microorganisms, aquatic flora and fauna, which in turn, may enter into the human food chain and result in health problems. For instance, chromium-poisoning causes skin disorders and liver damages. Chromium is usually encountered in the environment in the oxidation states of (III) and (VI). Each of the above oxidation states has very different biological and chemical properties. Cr(III) is considered to be a non-labile, inert element in the environment and essential for mammals in trace amounts, whereas Cr(VI) is much more labile, toxic and carcinogenic for a variety of organisms [1]. Due to its common presence in effluent discharge from steelworks, chromium electroplating, leather tanning and chemical manufacturing, chromium is often detected in sewage plants that combine industrial and municipal wastewater for treatment.

Besides, many heavy metals that have inhibitory or toxic effects on activated sludge microorganisms can upset the operation of the activated sludge process. Literature data on toxicity effects of Cr(VI) on activated sludge process are contradictory. Stasinakis et al. [2] reported that Cr(VI) concentrations equal or greater than 10 $mg\,L^{-1}$ inhibit the growth of unacclimatized activated sludge. Chromium at a sub-toxic level of 0.05 $mg\,L^{-1}$ affected the sequencing batch reactor performance to different extents depending on the hydraulic retention time [3]. Yetis et al. [4] reported stimulatory effects on biomass yield in the presence of 25 $mg\,L^{-1}$ Cr(VI).

The most commonly used technology for treatment of heavy metals in wastewaters is chemical precipitation. In the case of chromium, Cr(III) but not Cr(VI) may be removed from water as an insoluble chromium hydroxide. Recently, several Cr(VI) reducing bacterial species have been identified; these bacteria reduce the toxic hexavalent chromium to the less toxic and less mobile state Cr(III) utilizing a wide range of substrate at near neutral pH [5]. In addition, the reduction of Cr(VI) to Cr(III) using activated sludges under aerobic conditions has also been reported [6].

* Corresponding author. Tel.: +54 221 4254853; fax: +54 221 4254853.
E-mail address: econtrer@quimica.unlp.edu.ar (E.M. Contreras).

0304-3894/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2007.04.043

Adsorption with activated carbon is a widely used method to eliminate organic and inorganic contaminants in industrial wastewaters. The performance of the process is influenced by different parameters including the operating conditions, type of activated carbon and physicochemical characteristics of the wastewater. Several researchers [7,8] have studied the incorporation of powdered-activated carbon (PAC) in activated sludge systems for the treatment of complex liquid waste containing non biodegradable compounds and toxic or inhibitory substances to improve the performance treatment. However, information about the effect of PAC addition in activated sludge reactors for the treatment of wastewaters containing heavy metals is limited.

The objectives of the present study were: (a) to evaluate the removal of hexavalent chromium by (i) activated sludge microorganisms in aerobic batch reactors, (ii) powdered-activated carbon, and (iii) the combined action of powdered-activated carbon and biomass; (b) to propose mathematical models that interpret the experimental results.

2. Materials and methods

2.1. Biological and chemical materials

The biomass used in this work was cultured in a laboratory scale (4.5 L) activated sludge aerobic reactor. The plant was fed with synthetic wastewater containing dehydrated cheese whey: 1500 mg, $SO_4(NH_4)_2$: 94 mg and $NaHCO_3$: 1030 mg dissolved in 1 L of tap water. Hydraulic retention time was two days; sludge age was maintained at 45 days by daily wasting of the mixed liquor directly from the reactor. During the experiments the reactor temperature was kept at 20 ± 2 °C; under steady state conditions dissolved oxygen concentration was above 5 mg L^{-1}, pH was 7.5 ± 0.4, and soluble chemical oxygen demand (COD) ranged between 30 and 80 mg L^{-1}.

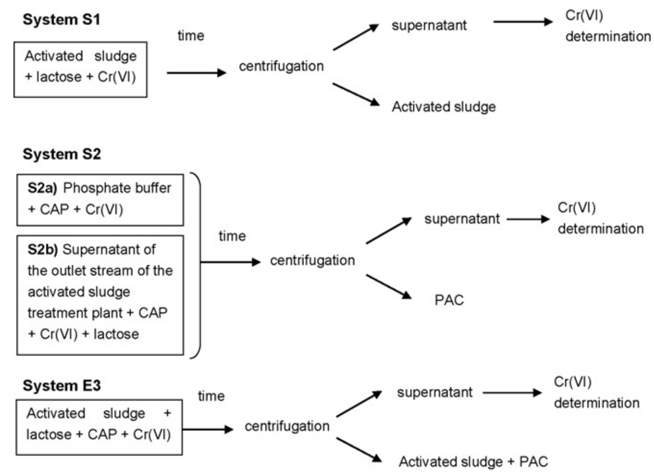
Cr(VI) stock solutions were freshly prepared using analytical grade $K_2Cr_2O_7$; tested Cr(VI) concentrations ranged between 10 and 100 mg L^{-1}. Powdered-activated carbon (PAC) concentrations between 0.5 and 8 g L^{-1} (Clarimex S.A., type 061) were tested. Table 1 shows the characteristics of the activated carbon used.

2.2. Chromium removal kinetics

Cr(VI) batch removal assays were performed in 0.5 L aerated vessels at constant temperature (20 ± 2 °C) and initial pH 7.0 ± 0.1; this pH was selected because it is the optimum value for the metabolic activity of most of the microorganisms that are present in a typical activated sludge. The initial Cr(VI) concentration ranged between 10 and 100 mg L^{-1}. Cr(VI) removal experiments were performed using different systems: (S1) activated sludge (biomass), (S2) PAC, (S3) biomass with the addition of activated carbon. Scheme 1 shows a representation of the performed experiments.

Table 1
Characteristics of the powdered-activated carbon (PAC) used

Properties	Value
Surface area, BET (N_2/77 K)	889 m^2 g^{-1}
Methylene blue adsorption	260 mg g^{-1}
Iodine adsorption	800 mg g^{-1}
Bulk density	0.29 g cm^{-3}
Moisture	12%
pH (1% suspension)	6.0–8.0
Screen analysis, passes mesh #325	60–80 wt%



Scheme 1. Scheme of the tested Cr(VI) removal systems.

In systems S1 and S3, where biomass was present, lactose was added as the carbon source in a concentration of 5 gCOD L^{-1}. This sugar was chosen as the electron donor because it was the main component of the cheese whey used to feed the activated sludge reactor. Previous works [9] showed that the presence of lactose was necessary for the biomass to remove Cr(VI). In systems S1 and S3, the biomass concentration was 2000 ± 300 mgCOD L^{-1}. In system S3 the PAC concentration used was 4 g L^{-1}, based on the reports of Lee et al. [10]. Experiment S2 was performed using two different media:

S2a phosphate buffer (NaH_2PO_4, 1 g L^{-1}; K_2HPO_4, 0.25 g L^{-1}) pH 7.0 ± 0.1 with PAC concentration ranging between 0.5 and 8 g L^{-1}.

S2b the supernatant of the centrifuged (13,000 rpm, 5 min Eppendorf centrifuge 5415C, Hamburg, Germany) and filtered (Cellulosic membranes, 0.45 μm OSMONICS INC.) outlet stream of the activated sludge treatment plant. In this case, lactose (5 gCOD L^{-1}) was added in order to have the same conditions than those found in the systems with biomass (S1 and S3); tested PAC concentrations ranged between 2 and 8 g L^{-1}.

At different time intervals samples were taken and were centrifuged to eliminate the biomass and/or PAC; then, the Cr(VI) concentration in the supernatant was determined. Hexavalent chromium was measured colorimetrically by reaction with diphenylcarbazide in acid solutions [11]. The absorbance was measured at 540 nm with a Hach spectrophotometer. Biomass concentration was measured as chemical oxygen demand [12] using a commercial kit (Hach). All assays were performed at room temperature (20 ± 2 °C).