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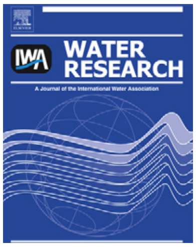

Biological Cr(VI) removal coupled with biomass growth, biomass decay, and multiple substrate limitation

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ABSTRACT

In this work, a mathematical model for the biological reduction of Cr(VI), carbon and nitrogen sources consumption, and biomass growth under fully aerobic conditions was developed. The model comprises three types of aerobic heterotrophic cells (non-growing cells, growing cells with chromate reductase activity, and growing cells that have lost the chromate reductase activity), and five soluble compounds (organic substrate, ammonia nitrogen, non-metabolizable soluble products, dissolved oxygen, and hexavalent chromium). Two processes are considered responsible for the reduction of Cr(VI). The first one is the reduction of Cr(VI) coupled with growth, the second process is coupled with the endogenous decay of the biomass. The model was calibrated using the results obtained in batch cultures in the absence of carbon and nitrogen sources, using different initial Cr(VI) concentrations (0–100 mgCr L^{-1}), two carbon sources (cheese whey and lactose), and different initial nitrogen to carbon ratio (0–50 mgN $gCOD^{-1}$). The calibrated model was used to calculate steady-state values of TSS, soluble COD, TAN and Cr(VI) in continuous systems, obtaining a good agreement with the experimental data. The model also accurately predicted the transient concentration of Cr(VI) as a function of time in response to step changes of the inlet Cr(VI) concentration in continuous systems.

1. Introduction

Biotransformation of metals is a promising technique to convert more toxic heavy metals into less toxic forms, and therefore, can be potentially useful for bioremediation of industrial wastewaters. A good example of biotransformation is the case of chromium.

The extensive use of chromium in several industries such as petroleum refining, metal finishing, leather tanning, iron and steel industries, inorganic chemical production, textile manufacturing and pulp production have largely contributed to its wide spread in the environment (Katz and Salem, 1994; Guertin et al., 2005). Although chromium has several oxidation states, chromium compounds mainly occur as Cr(III) or Cr(VI). The former is the most stable under reduced conditions, it is relatively immobile because it has a strong affinity for negative charged ions and colloids in soils, and gives sparingly soluble compounds such as $Cr(OH)_3$ that dominate at pH values from 4 to 8. Conversely, Cr(VI) is more soluble, mobile, and bio-available than Cr(III). Cr(VI) occurs in the form of oxoanions under most environmental conditions. Equilibria of hexavalent chromium compounds are pH and concentration dependent. Chromate ion (CrO_4^{2-}) represents more than 98% of the total Cr(VI) species for pH higher than 8. Chromate

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Nomenclature

Model compounds

Cr (mgCr L^{-1}) soluble hexavalent chromium concentration

S (mgCOD L^{-1}) organic substrate concentration

P (mgCOD L^{-1}) soluble products concentration released during the biomass decay

NH (mgN L^{-1}) total ammonia nitrogen (TAN) concentration

X_{NG} (mgCOD L^{-1}) non-growing biomass concentration

X_{GA} (mgCOD L^{-1}) growing active (with chromate reductase activity) biomass concentration

X_{GNA} (mgCOD L^{-1}) growing non-active (without chromate reductase activity) biomass concentration

Stoichiometric coefficients

Y (mgCOD $mgCOD^{-1}$) true biomass yield

$i_{N,BM}$ (mgN $mgCOD^{-1}$) nitrogen content of the biomass

$i_{N,P}$ (mgN $mgCOD^{-1}$) nitrogen content of the products released during the endogenous decay

f_P (mgCOD $mgCOD^{-1}$) fraction of the endogenous biomass converted into soluble inert products

R_C (mgCr $mgCOD^{-1}$) Cr(VI) removed per unit mass of X_{GA} converted into X_{GNA}

i_{SS} (mgTSS $mgCOD^{-1}$) conversion factor from biomass COD to TSS units

Kinetic coefficients

k_A (h^{-1}) first order lag phase constant

μ_{m0} (h^{-1}) maximum specific growth rate in the absence of Cr(VI)

$\mu_{m\infty}$ (h^{-1}) maximum specific growth rate at infinite Cr(VI)

q_{Sm0} (mgCOD $mgCOD^{-1}$ h^{-1}) maximum specific substrate consumption rate in the absence of Cr(VI)

$q_{Sm\infty}$ (mgCOD $mgCOD^{-1}$ h^{-1}) maximum specific substrate consumption rate at infinite Cr(VI) concentration

K (L $mgCr^{-1}$) inhibition constant due to Cr(VI) toxicity

K_S (mgCOD L^{-1}) half-saturation coefficient for S

K_{NH} (mgN/L) half-saturation coefficient for NH

b (h^{-1}) specific endogenous decay rate

q_{CrGm} (mgCr $mgCOD^{-1}$ h^{-1}) maximum specific Cr(VI) consumption rate associated to the growth phase

q_{CrDm} (mgCr $mgCOD^{-1}$ h^{-1}) maximum specific Cr(VI) consumption rate associated to the decay phase

monoacid ($HCrO_4^-$), and dichromate ($Cr_2O_7^{2-}$) ions are the main species when pH is lower than 5. In addition, as the total Cr(VI) concentration increases, the fraction of $HCrO_4^-$ decreases due to the formation of dichromate. In all cases, the fraction of chromic acid (H_2CrO_4) is negligible. Within the normal pH range of most biological wastewater treatment systems (pH about 5–9) and for Cr(VI) concentrations usually found in wastewaters (usually less than 2 mM), $Cr_2O_7^{2-}$ ion account for less than 3% of the total Cr(VI); thus, $HCrO_4^-$ and CrO_4^{2-} are the dominant species (Contreras et al., in press).

The reduction of Cr(VI) to Cr(III) is of great environmental importance, because Cr(III) is less hazardous. Chromium is an essential micro-nutrient in the diet of animals and humans, as it is indispensable for the normal sugar, lipid and protein metabolism of mammals (USEPA, 1998a). Conversely, Cr(VI) is highly toxic to all forms of living organisms, mutagenic in bacteria, mutagenic and carcinogenic in humans and animals (USEPA, 1998b). For these reasons, reducing Cr(VI) to Cr(III) is beneficial in eliminating the toxicity of Cr(VI) from the environment.

For many years, conventional Cr(VI) removal was achieved by chemical reduction, ion exchange or adsorption. Recently, researchers have focused attention on biodetoxification of hexavalent chromium. In contrast to the conventional methods, biodetoxification is cost-effective (Li et al., 2007). Trivalent and hexavalent forms of chromium can interconvert; within normal conditions, the reduction of Cr(VI) to Cr(III) due to the presence of organic compounds is favored. For example, the change of free energy at pH 7.0 and 25 °C corresponding to the reaction between acetic acid (electron donor) and chromate ion (electron acceptor) is about −83.3 kJ per mole of electrons transferred. Thus, from a thermodynamic point of view, Cr(VI) is capable of oxidizing acetic acid and also most of the organic compounds commonly found in wastewaters (Contreras et al., in press). However, the reduction of Cr(VI) to Cr(III) by organic compounds is frequently slow; thus, in the absence of a catalyst, such as the activated sludge biomass, redox systems are far from equilibrium (Stumm and Morgan, 1996). Therefore, the presence of cells that act as catalyst, and a suitable electron donor are necessary to achieve the reduction of Cr(VI).

The ability of Cr(VI) reduction has been found in many bacterial genera including *Pseudomonas*, *Micrococcus*, *Bacillus*, *Achromobacter*, *Microbacterium*, *Arthrobacter*, and *Corynebacterium* (McLean et al., 2000; Pattanapipitpaisal et al., 2001; McLean and Beveridge, 2001; Megharaj et al., 2003). The mechanisms through which bacterial strains reduce Cr(VI) to Cr(III) are variable and species dependent (McLean et al., 2000). Anaerobic bacteria may use chromate as a terminal-electron acceptor or reduce chromate in periplasmatic space by hydrogenase or cytocrome c3 (Michel et al., 2001; Puzon et al., 2002). In aerobic bacteria, Cr(VI) reduction may be carried out by cellular reducing agents (the primary reductant is glutathione) and NADH-dependent chromate reductase (Shen and Wang, 1994; Garbisu et al., 1998). The mechanisms for Cr(VI) reduction might be a secondary utilization or cometabolism as suggested for *Shewanella onoidensis* MR-1 (Middleton et al., 2003).

Although there are many studies concerning the removal of Cr(VI) by pure cultures of different microorganisms, its applicability to field removal processes is limited. The main disadvantage of using pure cultures to remove chromium compounds is related to the use of sterile conditions to prevent external microbial contamination, increasing the treatment costs. If sterile conditions are not employed (due to economic reasons, for example), indigenous bacteria may overcome the added Cr(VI)-reducing microorganisms. Besides, most countries have severe restrictions concerning the introduction of new species. For these reasons, results obtained in the study of Cr(VI) removal by mixed cultures,