Kinetic assessment of simultaneous removal of arsenite, chlorate and nitrate under autotrophic and mixotrophic conditions

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HIGHLIGHTS

- A model was proposed to simulate simultaneous removal of As (III), ClO_3^- and NO_3^-.
- Autotrophic and mixotrophic modes significantly affected the removal efficiency.
- HRT and input COD concentration significantly impacted the removal efficiency.
- Above 90% of As (III), ClO_3^- and NO_3^- can be removed under optimal conditions.

GRAPHICAL ABSTRACT
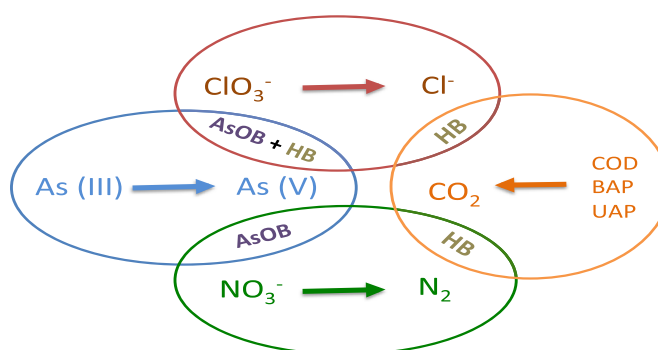
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ABSTRACT

In this work, a kinetic model was proposed to evaluate the simultaneous removal of arsenite (As (III)), chlorate (ClO_3^-) and nitrate (NO_3^-) in a granule-based mixotrophic As (III) oxidizing bioreactor for the first time. The autotrophic kinetics related to growth-linked As (III) oxidation and ClO_3^- reduction by As (III) oxidizing bacteria (AsOB) were calibrated and validated based on experimental data from batch test and long-term reactor operation under autotrophic conditions. The heterotrophic kinetics related to non-growth linked As (III) oxidation and ClO_3^- reduction by heterotrophic bacteria (HB) were evaluated based on the batch experimental data under heterotrophic conditions. The existing kinetics related to As (III) oxidation with NO_3^- as the electron acceptor together with heterotrophic denitrification were incorporated into the model framework to assess the bioreactor performance in treatment of the three co-occurring contaminants. The results revealed that under autotrophic conditions As (III) was completely oxidized by AsOB (over 99%), while ClO_3^- and NO_3^- were poorly removed. Under mixotrophic conditions, the simultaneous removal of the three contaminants was achieved with As (III) oxidized mostly by AsOB and ClO_3^- and NO_3^- removed mostly by HB. Both hydraulic retention time (HRT) and influent organic matter (COD)

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concentration significantly affected the removal efficiency. Above 90% of As (III), ClO_3^- and NO_3^- were removed in the mixotrophic bioreactor under optimal operational conditions of HRT and influent COD.

1. Introduction

Arsenic (As) is widely spread in the upper earth crust at very low concentrations (Mukhopadhyay et al., 2002). However, the arsenic level has been significantly increased due to the intensive anthropogenic activities (i.e. mining, fossil fuel combustion, the consumption of arsenical products, etc.) (Smedley and Kinniburgh, 2002). The arsenic contaminated groundwater can cause acute environmental and healthy issues. Dietary uptake of arsenic compound potentially increased the risk of various disease due to its toxic, mutagenic and carcinogenic impact (Rahman et al., 2014). Arsenite (As (III)) and arsenate (As (V)) are the most common oxidation states of As in aquatic environment. Compared to As (III), As (V) is not only less mobile and toxic, but also can be adsorbed to a much greater capacity under environmentally relevant equilibrium concentrations (Lin and Puls, 2000; Oremland and Stolz, 2003; Sun et al., 2009a, 2009b; Wang et al., 2017). Researchers are focusing on the As (III) oxidation process to enhance the As immobilization.

Microbial oxidation of As (III) to As (V) by heterotrophic and chemoautotrophic bacteria has been demonstrated under aquatic circumstance (Gihring et al., 2001; Oremland et al., 2002; Rhine et al., 2006; Sun et al., 2010a; Sun et al., 2010), mediated by arsenite oxidase, a periplasmic enzyme (Silver and Phung, 2005). As (III) can be enzymatically converted to the less toxic As (V) as a detoxification mechanism by heterotrophic microorganisms (Pous et al., 2015). Autotrophic As (III) oxidizing bacteria (AsOB) can utilize the energy and reducing power from As (III) oxidation for CO_2 fixation and biomass synthesis (Rhine et al., 2006). In terms of in situ bioremediation of As contaminated groundwater, a very limited oxygen level is normally anticipated due to its low solubility and its potential reactions with reduced compounds (Almasri and Kaluarachchi, 2004). Nitrate (NO_3^-), the most ubiquitous chemical contaminant in groundwater (Peng et al., 2015a, 2015b), would be an alternative electron acceptor under anoxic conditions. Coupled As (III) oxidation and NO_3^- reduction has been extensively studied using isolated pure culture (Rhine et al., 2006), enriched denitrifying culture (Sun et al., 2009a, 2009b) and granular sludge (Sun et al., 2010a). Continuous flow reactors were also designed and operated with the aim to completely immobilize As by adsorption onto activated alumina (Sun et al., 2010) and biogenic ferric (hydr)oxides (Sun et al., 2009a, 2009b).

Chlorate (ClO_3^-) is one of the serious oxidized contaminants in groundwater. ClO_3^- contamination primarily originates from production of herbicides and bleaching agents (Gordon and Tachiyashiki, 1991). ClO_3^- is one of the reduced products from perchlorate (ClO_4^-) and appears to be more toxic than ClO_4^- (Anderson et al., 2000). Many microorganisms have been isolated so far to utilize ClO_3^- as electron acceptor (Carlström et al., 2015). The biochemical reduction steps by ClO_3^- reducing bacteria (CRB) are analogous to those by ClO_4^- reducing bacteria (PRB) (Clark et al., 2015). Microbial reduction of ClO_4^- generally proceeds via a sequential processes from ClO_4^- to Cl^-, via ClO_3^- and ClO_2^- as intermediates (Coates and Achenbach, 2004). The reductions of ClO_4^- to ClO_3^- and ClO_3^- to ClO_2^- are mediated by (per)chlorate reductase (Kengen et al., 1999). Recently, Sun et al. (2010b) demonstrated that ClO_3^- could be used as a alternative electron acceptor to enhance As (III) oxidation using both autotrophic and heterotrophic enriched culture under batch conditions. Furthermore, simultaneous removal of As (III) and ClO_3^- by granular sewage sludge was also achieved in an up-flow anaerobic sludge bed (UASB) bioreactor (Sun et al., 2011).

Mathematical models have been widely used to predict substrate dynamics in both autotrophic and heterotrophic processes. To date, different models have been proposed to study the kinetics of As (III) oxidation and (per)chlorate reduction, individually. For example, Peng et al. (2017) integrated oxidation of As (III) and ferrous iron, coupled to NO_3^- reduction, ferric iron precipitation and As (V) adsorption process into one model framework and successfully applied it in granular systems with varying configuration and conditions. Simultaneous reduction of NO_3^- and ClO_4^- in the hydrogen-based membrane biofilm reactor was also assessed using a multispecies biofilm model (Tang et al., 2012). The first-order kinetic constants of ClO_3^- reduction were estimated based on sediments samples from a wetland (Schwarz et al., 2012). Nevertheless, multiple contaminants (e.g., As (III), ClO_3^- and NO_3^-) may generally co-exist in groundwater. It is known that AsOB possess the capability to remove As (III) (Zhang et al., 2015), ClO_3^- (Sun et al., 2010b) and NO_3^- (Sun et al., 2009a, 2009b). However, none of the existing models are able to describe the interactions among these contaminant substrates as well as the microbes during the remediation process.

In this work, we aim to develop a comprehensive mathematical model incorporating As (III) oxidation, ClO_3^- reduction and NO_3^- reduction by both autotrophic and heterotrophic bacteria for the first time. We firstly calibrated the proposed model kinetics by best-fitting data from batch experiments and continuous operation of lab-scale bioreactors under autotrophic or heterotrophic conditions. We then used the validated model and the obtained kinetic values to investigate the mechanistic interactions among microorganisms performing ClO_3^- and NO_3^- reduction as well as As (III) and organic matters (COD) oxidation under autotrophic and mixotrophic conditions. The modeling data were also used to interpret the combined effect of two key operating parameters (i.e., hydraulic retention time (HRT) and influent COD) on the simultaneous removal of the three contaminants in a mixotrophic granular reactor.

2. Materials and methods

2.1. Model development for biological processes

The proposed model framework for biological processes involves multiple-substrate Monod kinetics consisting of 8 soluble growth substrates and 4 solid components. The soluble substrates are ClO_3^-, Cl^-, As (III), As (V), NO_3^-, soluble COD (S_S), substrate-utilization-associated products (UAP), and biomass-associated products (BAP). UAP results from intermediates or end products of substrate degradation, cell metabolism, or cell growth, while BAP is a result of endogenous respiration, i.e., cell lysis and decay (Boero et al., 1991). The solid components are extracellular polymeric substances (EPS), AsOB, heterotrophic bacteria (HB), inert biomass (X_I). In total, 16 biological processes are considered in this model, including growth of AsOB on As (III) + NO_3^- or As (III) + ClO_3^-; growth of HB on COD + NO_3^-, COD + ClO_3^-, UAP + NO_3^-, UAP + ClO_3^-, BAP + NO_3^- or BAP + ClO_3^-; concomitant As (III) oxidation by HB; endogenous respiration of AsOB on NO_3^-/ClO_3^-; AsOB inactivation; endogenous respiration of HB on NO_3^-/ClO_3^-; HB inactivation and EPS hydrolysis. Energy gained from the oxidation/reduction reactions is used for production of biomass, UAP and EPS. Hence, the model routes the electrons from As (III) and COD via three pathways: i) EPS production (fraction denoted as α_1); ii) UAP production (fraction denoted as α_2); iii) AsOB or HB synthesis (fraction denoted as α_3). The mass balance requires that $\alpha_1 + \alpha_2 + \alpha_3 = 1$. Endogenous respiration converts part of the active biomass and the electron acceptors for energy of cell maintenance, while the inactivation of microorganisms generates