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The rapid adsorption-microbial reduction of perchlorate from aqueous solution by novel amine-crosslinked magnetic biopolymer resin

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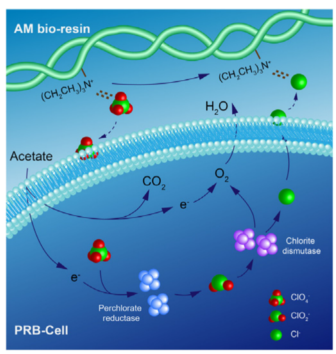
HIGHLIGHTS

- Amine-crosslinked magnetic biopolymer resin was prepared for perchlorate uptake.
- This study provides a rapid adsorption-microbial reduction for perchlorate.
- Perchlorate removal by resin mainly includes ion exchange and physical absorption.
- This novel bio-adsorbent could achieve rapid separation from effluents.
- Reduction time, pH and biomass affect efficiency of microbial regeneration obviously.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this work was to study the adsorption characters of resin, microbial reduction of perchlorate and combined process of perchlorate removal in aqueous solution. Study demonstrated the adsorption equilibrium was achieved in 120 min, which based on ion exchange reaction. Dissolved perchlorate (100 mg/L) can be completely removed by acclimated anaerobic sludge in 15 h, and the concentrated perchlorate (~200 mg/g) on the surface of resin would be effectively microbial reduced after 3 days. Neutral environment (pH = 7.4), higher biomass and additional electron donor can apparently improve the biological reduction efficiency of concentrated perchlorate. Addition of many co-anions showed the competition adsorption towards perchlorate, especially in the presence of NO_3^-. This study provides an effective method for perchlorate reduction by the adsorption-microbial process.

1. Introduction

Perchlorate (ClO_4^-) has a strong oxidizing character and are commonly used in manufacturing of rocket propellants, pyrotechnic devices and missiles since the 1950s (Zhao et al., 2011). Due to its high solubility, lethargic reactivity and low adsorption to natural solids, increasing amounts of perchlorate have existed in public groundwater, surface water, soil and food all over the world (Choe et al., 2013).

Since the structural similarity to iodide (charge and ionic radius), perchlorate is a thyroid endocrine disruptor and affects human health at low concentration. For fetuses and young children, perchlorate can inhibit the uptake of iodide and then affects thyroid hormone production, which results in stunted growth and mental retardation (Ha et al., 2011). In adults, the less of hormones would lead to potential neurotoxic symptom that is essential for neurodevelopment (Kumarathilaka et al., 2016). It's worth noting that including Antarctica (Jackson et al., 2012), China (Wu et al., 2010), United States (Kalkhoff et al., 2010; Plummer et al., 2006; Urbansky, 2002), Germany (Scheytt et al., 2011), Canada (Backus

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et al., 2005), Israel (Gal et al., 2009), South Korea (Quinones et al., 2007), Japan (Kosaka et al., 2007) and India (Kannan et al., 2009) have detected non negligible level of perchlorate in the groundwater and/or surface water, soil and food already. To protect human health, many states and cities in America have implemented the regulatory standards for perchlorate contaminant, such as California (6 μg/L), Massachusetts (2 μg/L), Arizona (14 μg/L) and New York (5 μg/L). In 2011, the U.S. EPA made a determination to set a federal regulatory standard for controlling the perchlorate in drinking water (Azizi et al., 2011).

Under most environmental conditions, the stable physical and chemical nature of perchlorate makes it difficult to be treated in the aqueous solution. Once dissolved, the ClO_4^- anion with the +7 oxidation state will persist in the environment for a long time since the high activation energy necessary for reduction (Kumarathilaka et al., 2016). Currently, available technologies have been used for removing perchlorate from water, including physical adsorption, ion exchange, membrane filtration, situ/ex-situ biodegradation with microorganisms, and catalytic reduction (Kim and Choi, 2014). Among these methods for perchlorate removal, ion exchange is recognized as the most commonly technology in the world (Xiao and Roberts, 2013). In California and Massachusetts, the over two dozen plants were utilized to treat perchlorate by ion exchange technology (Choe et al., 2013). Although the ion exchange can be used to extract perchlorate from water effectively and conveniently, they also need further treatment for frequent resin regeneration and spent regenerant brine disposal. Meanwhile, the hard separation of traditional adsorbent is also the issue to restrict the development of this technology. Similarly, biological treatment has potential eco-friendly ability for reducing perchlorate contaminant, which can stepwise reduce perchlorate to chloride and oxygen by two cell-bound enzymes. But the low kinetics, extremely sensitive to temperature and pH changes, and low-concentration of ClO_4^- are required to pay more attention in the application of real environment (Kumarathilaka et al., 2016). Therefore, the significant obstacles are exist for applying this technology in the large scale.

In this work, in order to overcome the issue of adsorbent separation and increase the capacity of perchlorate removal, Fe_3O_4 nanoparticles and amine functional groups were introduced into the raw corn stalk forming the amine-crosslinked magnetic biopolymer resin (AM bio-resin). Meanwhile, after the process of adsorption, microbial treatment was used to reduce the concentrated perchlorate on the resin, and then achieved the goal of adsorbent regeneration and perchlorate elimination. The objectives of this study were to evaluate the adsorption capacity of the novel biopolymer resin for perchlorate, and developed a new adsorption-microbial reduction method to remove perchlorate from the aqueous solution. Our work showed that, the adsorption capacity of resin for perchlorate is 232.56 mg/g at 293 K based on the Langmuir model. Predominant removal mechanisms of adsorption are physical absorption and ion exchange reaction between Cl-containing groups and ClO_4^-. Meanwhile, the perchlorate reducing bacteria (PRB) can be easily obtained from activated sludge by artificial domestication for several weeks. This microbial regeneration method for resin is effective, environmentally-friendly and convenient to control in realistic condition.

2. Materials and methods

2.1. Reagents and microorganisms

Corn stalk was collected from Liaocheng (Shandong, China) and sieved into particles with diameters 100–200 μm. All the primary chemicals in this study were used as received and purchased from Tianjin Damao Chemical Reagents Company (Tianjin, China). The pH of the solutions was adjusted with NaOH (0.1 mol/L) and HCl (0.1 mol/L).

Microorganism seeds were obtained from activated sludge of G. domestic sewage treatment plant (Jinan, Shandong, China). After acclimation and related test for two months, the concentration of perchlorate in the SBR effluent was detected less than 1 μg/L (initial concentration of 0.5 g/L), which indicated the acclimation achieving of anaerobic sludge with perchlorate reducing bacteria (PRB). Then the PRB, which mixed in the acclimated anaerobic sludge, were sent to *Novogene* Biological Information Technology Co., Ltd. (Beijing, China) for 16S rDNA sequence analysis. The acclimated anaerobic sludge were used in whole experiments except for the seed of acclimation period. The culture medium for PRB enrichment contained the following components per liter: NaH_2PO_4 (1.4 g), $(NH_4)_2SO_4$ (0.1 g), $MgSO_4$ (0.1 g), $FeSO_4$ (4.0×10^{-3} g), $Na_2MoO_4{\cdot}2H_2O$ (0.6×10^{-3} g), $NaSeO_3$ (1.0×10^{-3} g), H_3BO_3 (0.6×10^{-3} g), CH_3COONa (1.0 g) and $NaClO_4$ (0.5 g). Furthermore, NaOH and HCl were added into the medium to adjust the pH to 7.0. The specific enrichment method and operation process can be found in our previous works (Song et al., 2015b).

2.2. Preparation and analysis of AM bio-resin

AM bio-resin was prepared by a two-step synthesis method as the previous reports (Song et al., 2016). Firstly, a solution containing $FeCl_3$ (0.15 mol/L) and $FeSO_4$ (0.075 mol/L) was prepared with deionized water. Then the virgin corn stalk (1.5 g) was magnetized by co-precipitation process with the mixed iron solution. Secondly, the magnetized corn stalk were reacted with epichlorohydrin, N,N-dimethylformamide, ethylenediamine and trimethylamine to introduce amine and other functional group. After washing with deionized water and drying at 353 K for 4 h, the products were obtained and named AM bio-resin.

The virgin corn stalk and AM bio-resin were analyzed with FTIR spectroscopy (Perkin–Elmer "Spectrum BX" spectrometer), scanning electron microscopy (NoVa™ Nano SEM 250), transmission electron microscopy (TEM, FEI Tecnai G20), Zeta potential measurement (Malvern Zetasizer NANO ZS), vibrating sample magnetometry (MPMS-XL-7 Quantum Design) and X-ray photoelectron spectroscopy (Thermo ESCALAB 250XI).

2.3. Batch adsorption of perchlorate on AM bio-resin

Batch adsorption tests for perchlorate removal were carried out in a 100 mL Erlenmeyer flask by introducing 0.1 g AM bio-resin into 100 mL $NaClO_4$ solution. The mixture was stirred in a shaking bath with a speed of 160 rpm. Adsorption kinetics were studied over the range of 0–360 min with three initial concentration of perchlorate (50, 100, 200 mg/L) at 293 K. Pseudo first order model, modified pseudo first order model, pseudo second order model and intraparticle diffusion model were carried out to investigated the adsorption kinetics of perchlorate. Adsorption isotherms were conducted by shaking 0.1 g AM bio-resin with 100 mL perchlorate solution at pH 7 for 4 h. The temperatures of isotherms were selected as 293 K, 303 K and 313 K. Langmuir model, Freundilich model and Temkin model were carried out to analyze the adsorption isotherms process. All the samples were collected and filtered by microfiltration membrane (0.22 μm) to analyze the residual perchlorate concentration.

2.4. Dissolved perchlorate reduction by microorganisms

To determine the perchlorate reduction ability of microorganisms used in this study, 50 mL acclimated anaerobic sludge (MLSS = 3.56 g/L, SVI = 50.1 mL/g) was mixed with 50 mL