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# Treatment of dissolved perchlorate by adsorption–microbial reduction

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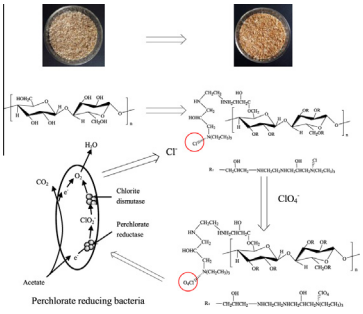
## HIGHLIGHTS

- Adsorption combined with biological reduction was used for perchlorate elimination.
- Phylogenetic tree was performed for analyzing the predominant strains.
- The optimum pH for high bio-regeneration efficiency was found at 7.3(±0.1).
- The column adsorption of perchlorate by BBA followed the Thomas model.
- The process achieved bio-regeneration of adsorbent and reduction of perchlorate.

## GRAPHICAL ABSTRACT

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## ABSTRACT

A novel method for perchlorate reduction by combination of adsorption and biological reduction was investigated in this work. After being adsorbed by biosorbent, the concentrated perchlorate was completely biologically reduced by mixed bacteria, which were dominated by Proteobacterial species. The reducing efficiency of perchlorate concentrated on biopolymer based adsorbent surface achieved optimal (75–85%) after 4 days of reduction time in the neutral environment (pH: 7.0–7.5). The reduction of perchlorate was enhanced by the $Cl^-$ and $SO_4^{2-}$ ions and weakened by the dissolved $NO_3^-$ ions in the reduction system. Moreover, per gram biopolymer based adsorbent could uptake 134.9 and 102.4 mg of perchlorate in the first and second bio-regeneration cycles of column tests, with regeneration efficiency of 77.7% and 59.0%, respectively. In conclusion, results indicated that the reduction of concentrated perchlorate could be achieved simultaneously with the biosorbent bio-regeneration.



## 1. Introduction

Perchlorate is widely used in manufacture of rocket propellants, missiles, road flares automobile airbags and fireworks, which would finally enters the water resources [1,2]. According to previous toxicological studies, perchlorate has a direct effect on thyroid gland iodine uptaking; furthermore, megadose of perchlorate may cause fatal bone marrow disorders [3,4]. As reported by United States Environmental Protection Agency (USEPA), the drinking water of at least 15 million people in the United States was affected by perchlorate contamination [5]. Therefore, perchlorate was added in the drinking water candidate contaminant list (CCL) of USEPA in 1998. Moreover, USEPA further adopted a new drinking water standard of 24.5 μg/L for perchlorate in 2005 [6]. Perchlorate ($ClO_4^-$) contamination is highly soluble, nonvolatile and kinetically inert in the surface and ground water bodies [7,8]. Thus, only few technologies would be necessary for efficient and environmental removal of perchlorate. Previously, anion exchange and membrane technology were used widely in the perchlorate removal, remediation and destruction. However, these two categories of technologies could not only remove perchlorate

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from water, but also generate the contaminated adsorbent or membranes which need to be further treated [9]. Recently, several thermodynamic studies have predicted that perchlorate could be removed by reducing agents. However, due to the large kinetic barrier in natural environment, perchlorate is difficult to be removed by chemical reduction. Additionally, the technology of biological treatment has been proven useful for perchlorate destruction. Biological reduction, in which perchlorate reducing bacteria (PRB) uses perchlorate as the electron acceptor, is recognized as the most promising technology to remove perchlorate in the water supply [10]. A number of studies have indicated that PRB represent a broad phylogeny of Proteobacteria strain, which is the most widely distributed strains in the environment [11,12]. The single enzyme of PRB could reduce perchlorate to chlorate ($ClO_3^-$) and then to chlorite ($ClO_2^-$). Afterwards, the chlorite dismutase of PRB could further converts chlorite into chloride and molecular oxygen for perchlorate destructing [7,13]. However, the process of pure bio-reduction is relatively slow and extremely sensitive to pH/salinity for treating large-volume perchlorate contaminating water. In order to sustain the microbial activity, biological reduction still requires extra organic substrate and nutrient salts which always need a further treatment [14]. Nevertheless, hybrid technology would overcome the problems mentioned above, because the perchlorate could be concentrated on the adsorbent for further biological reduction. Compared with pure biological treatment, the hybrid technology can improve perchlorate reduction and produce less excess biomass [1]. Tan [15] has reported the uptake of perchlorate from aqueous solution by wheat straw based adsorbent. Though the subsequent biological regeneration was discussed at the end of research, the microbial characteristics, specific mechanism and influence factors of biological reduction were not involved, and need to be further improved.

In this research, ion exchange subsequently incorporated with biological reduction was found to be efficient and environmental for perchlorate elimination. After being adsorbed by biopolymer based adsorbent (BBA), the concentrated perchlorate was then deoxidized by PRB under anaerobic conditions. The BBA was prepared from modified wheat stalk by amination reaction with epichlorohydrin, ethylenediamine and triethylamine [16,17]. PRB were obtained from the cultivated anaerobic sludge collected from the wastewater treatment plant. At meantime, phylogenetic analysis of the predominant perchlorate reducing strain in the mixed cultivated sludge was also performed by online BLAST tool. All reduction conditions, such as the reduction time, pH, co-anions and biomass concentration in reduction system were optimized, so as to evaluate the optimal conditions for the concentrated perchlorate reduction by PRB. Finally, a series of column adsorption with bio-regeneration technology was discussed for analyzing the character of dynamic perchlorate removal process.

## 2. Materials and methods

### 2.1. Preparation of modified wheat stalk adsorbent

The BBA was prepared as our previous method with some minor modifications [15]. Firstly, the raw wheat stalk was washed with deionized water and dried in an oven at 105 °C for 24 h. Secondly, the raw wheat stalk (8 g), epichlorohydrin (10 mL), N,N-dimethylformamide (10 mL), ethylenediamine (3 mL) and triethylamine (8 mL) were mixed and reacted in a flask at 100 °C for 5 h. After this, epichlorohydrin, ethylenediamine and triethylamine were introduced into the framework of biopolymer based adsorbent, forming the positively quaternary amine group with nitrogen content of 8.45% ($-CH_2CHOHCH_2NHCH_2CH_2NHCH_2OHCHCH_2N(CH_2CH_2)_3^+$) (Fig. 1) [6]. After the reaction above, the obtained product was washed with NaOH (0.1 mol/L), HCl (0.1 mol/L), $C_2H_5OH$ (50%) and NaCl (0.1 mol/L), respectively. Finally, the BBA was dried at 60 °C for 12 h and sieved to desired mesh size (0.1–0.2 cm) for use.

### 2.2. Reagents

All the primary chemicals used in this study were analytical grade and purchased from Tianjin Damao Chemical Reagents Company (Tianjin, China). All solutions required were obtained by successive dilutions of the stock standard solution. The pH of solution was adjusted with NaOH (0.1 mol/L) and HCl (0.1 mol/L).

### 2.3. Perchlorate reducing bacteria

#### 2.3.1. Enrichment of perchlorate reducing bacteria

The perchlorate reducing bacteria were obtained from anaerobic sludge of a pulp and paper wastewater treatment plant in Zibo, Shandong, China. The gravity-settled sludge, which had no coarse solid particles, was used as the seed of heterotrophic perchlorate reducing bacteria in this study. The fresh culture medium for PRB enrichment was adjusted to neutral by NaOH (1 mol/L) and kept anoxic by purging with free-oxygen nitrogen. The basal culture medium contained (per liter) 1.44 g $NaH_2PO_4$, 0.1 g $(NH_4)_2SO_4$, 0.1 g $MgSO_4$, 4.0 mg $FeSO_4$, 0.6 mg $Na_2MoO_4{\cdot}2H_2O$, 1.0 mg $NaSeO_3$ and 0.6 mg $H_3BO_3$. $C_2H_3O_2^-$ (1000 mg/L) and $ClO_4^-$ (500 mg/L) were added into the medium as electron donor and acceptor [18]. A double organic-glass cylinder with effective volume of 4 L was used as the sealed container for PRB cultivating. During each cycle of cultivation, the seed (500 mL) and culture medium (3 L) were mixed in the container with magnetic stirring for 23 h at 30 °C. After an hour of settling down, 2.5 L of the supernatant was removed and replaced by fresh culture medium. After the cycles of 35 days, the concentration of cultivated sludge reached the goal amount of 9 g/L.

#### 2.3.2. Reduction of dissolved perchlorate by perchlorate reducing bacteria

To investigate the reduction ability of PRB for perchlorate, 50 mL of acclimated anaerobic sludge was mixed with 50 mL of fresh culture medium (with 50 mg/L of perchlorate) in a 250 mL sealed container. After shaking in an orbital incubator for 0, 4, 6, 9, 11, 24 and 27 h (180 rpm, 30 °C), the residual concentrations of perchlorate in the solution were detected by ion chromatograph (ICS-900, Dionex).

#### 2.3.3. Analysis of perchlorate reducing bacterial community

The isolated pure bacterial strains obtained from the acclimated anaerobic sludge was sent to Human Genome Center in Shanghai for 16S rDNA sequence analysis, and then the results were submitted to GenBank database to align by online BLAST tool. To represent the relationship between the predominant strains of acclimated anaerobic sludge and the known related genera, a neighbor-joining phylogenetic tree was generated by inserting 15 sequences of the predominant strains in this study and 2 sequences of the known perchlorate reducing strains.

### 2.4. Reduction of perchlorate

#### 2.4.1. Adsorption of perchlorate by modified wheat stalk

Adsorption studies were carried out by using 0.2 g BBA in 50 mL suspension solution containing 1000 mg/L $ClO_4^-$ in 100 mL Erlenmeyer flasks. After stirring for 12 h, the samples were filtered by microfiltration membrane of 0.45 μm, and then the residual $ClO_4^-$ ions in liquid samples were detected by ion chromatograph