



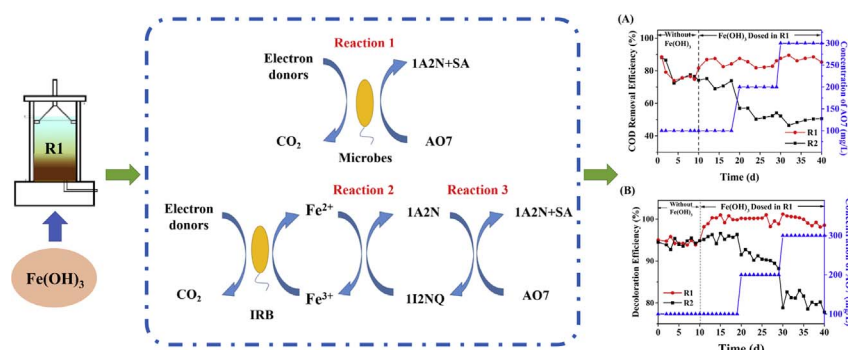
Promoting electron transfer to enhance anaerobic treatment of azo dye wastewater with adding $\text{Fe}(\text{OH})_3$



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GRAPHICAL ABSTRACT



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ABSTRACT

In this study, $\text{Fe}(\text{OH})_3$ was dosed into anaerobic reactor (R1) to stimulate the electron transfer process during the decoloration treatment. As results indicated, the chemical oxygen demand (COD) removal and decoloration efficiency were increased by 61.7% and 32.0% than that of the control reactor (R2), respectively. The cyclic-voltammetric analysis of the effluent demonstrated that the cycles of $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ and 1-imino-2-naphthol/1-amino-2-naphthol (oxidative/reductive state of the decoloration intermediate product) had been established in R1. The concentration of cytochrome c and the conductivity of suspended sludge in R1 were also 3.2 and 2.1 times higher than that in R2. All experiments above indicated that the electron transfer process between substrates and azo bonds was accelerated efficiently. Furthermore, the abundance of iron reducing bacteria was higher than that of R2, indicating that dissimilatory iron reduction as a reason for the $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ cycle played an important role in the anaerobic decoloration treatment.

1. Introduction

Acid Orange 7 (AO7) is a common azo dye that is widely used in coloring and printing of wool, leather, silk and nylon (Fernando et al., 2012). Due to the difficulty in biodegradation and biotoxicity, more effective means of treatment are required to treat wastewater containing AO7. Compared with the aerobic process, anaerobic technology

is preferred for AO7 treatment because oxygen can compete with azo bond to capture electrons to impede the azo degradation under aerobic conditions. In anaerobic processes, azo bond of AO7 was cleaved via azo reduction to produce colorless 1-amino-2-naphthol (1A2N) and sulfanilic acid (SA) as the intermediate products. 1A2N was reportedly capable of serving as a redox mediator that catalyzes the azo decoloration and forming its oxidation state 1-imino-2-naphthoquinone

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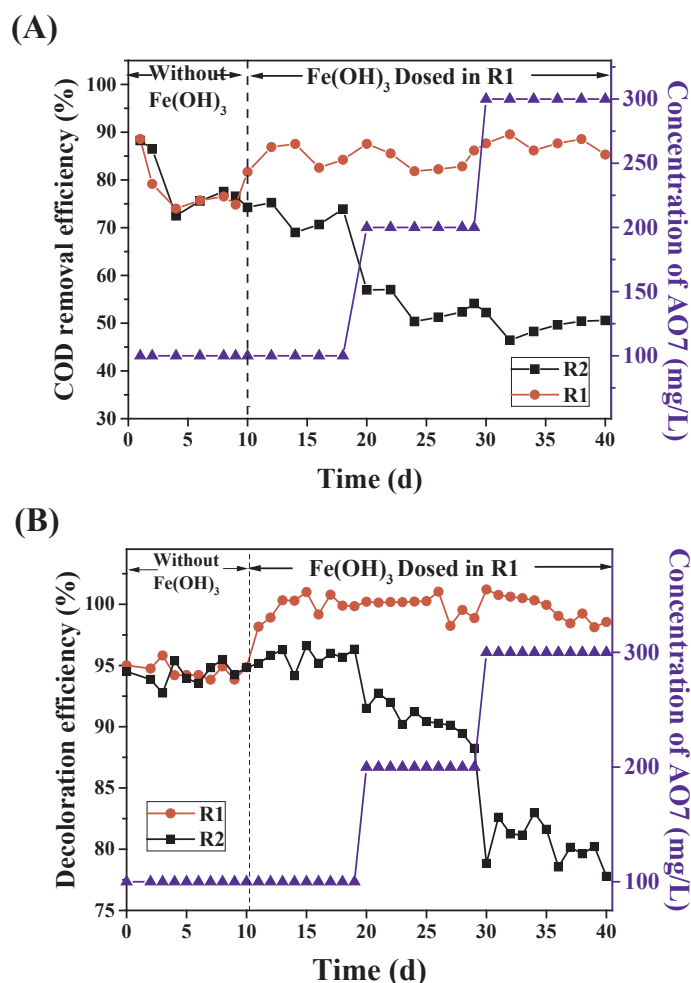


Fig. 1. Influence of $\text{Fe}(\text{OH})_3$ Powder on (A) COD Removal efficiency, (B) Decoloration efficiency.

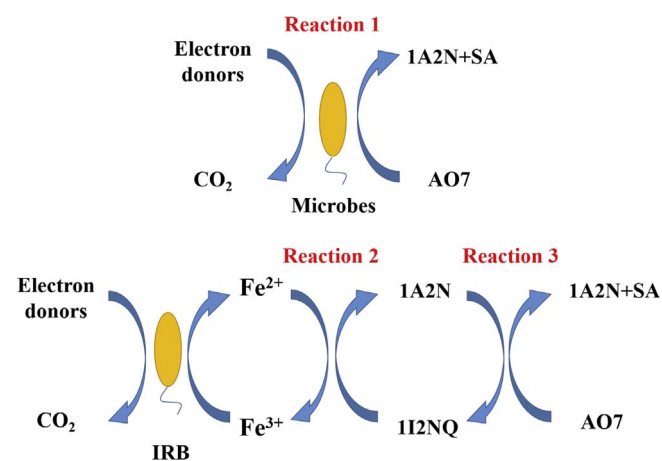


Fig. 2. The schematic diagram of three major reactions, including biotic (reaction 1), abiotic (reaction 3) decoloration of AO_7 and reduction of $1\text{I}2\text{NQ}$ by Fe^{2+} .

($1\text{I}2\text{NQ}$) (Méndez-Paz et al., 2005; Ong et al., 2006; Van der Zee et al., 2000; Xu et al., 2014). However, $1\text{I}2\text{NQ}$ could not be reduced chemically so that the efficiency of autocatalysis is limited. Therefore, it is desired to improve the electron transfer cycle of $1\text{I}2\text{NQ}/1\text{A}2\text{N}$ to enhance the dye decoloration as well as COD decomposition.

Dissimilatory iron reducing bacteria (IRB) were reported to play an important role in terminal electron accepting process in many anaerobic environments (Lovley, 1987). Both soluble and insoluble $\text{Fe}(\text{III})$ were used as electron acceptors for IRB to oxidize complex organic

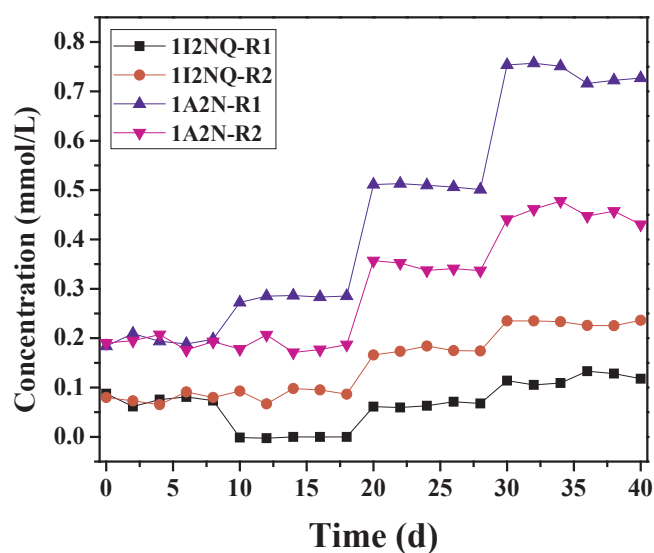


Fig. 3. Concentration of 1-imino-2-naphthoquinone ($1\text{I}2\text{NQ}$), which is the oxidation state of one of the main intermediate products, and the theoretical concentration of 1-amino-2-naphthol ($1\text{A}2\text{N}$) during the decoloration of AO_7 .

compounds. The transfer of electrons from electron donors by microbes to $\text{Fe}(\text{III})$ can be divided into direct and mediated electron transfer. Several IRB such as *Geobacter*, *Shewanella* and *Rhodospirillum rubrum* are capable of direct electron transfer via cytochrome c (Van der Zee and Cervantes, 2009). Other IRB could utilize self-generated redox mediators to

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