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Rapid reductive degradation of azo and anthraquinone dyes by nanoscale zero-valent iron

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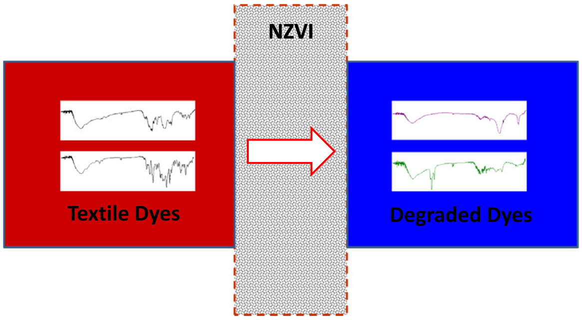
HIGHLIGHTS

- Reactive azo dye Remazol Brilliant Orange 3RID (RBO3RID) was removed using nanoscale zero-valent iron (NZVI) particles. Dye concentrations varies from 100 to 500 mg/L. NZVI could remove up to 2757 mg of RBO3RID dye. More than 80% dye removal was achieved within the first 15 minutes of reaction.
- Anthraquinone dye Reactive Blue MR (RBMR) was removed using NZVI particles. Dye concentrations varies from 100 to 500 mg/L. NZVI could remove up to 2207 mg of RBMR dye. More than 80% dye removal was achieved within the first 15 minutes of reaction.
- Dyes degraded up to 97% (NZVI dosages varied from 0.15 to 0.3 g/L).
- pH range used in the study was 2–12 and NZVI worked the best at pH = 8–12 which is the typical range of pH in textile wastewater.

GRAPHICAL ABSTRACT



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ABSTRACT

The presence of residual dyes in textile effluent is not desired as they are very toxic to the ecosystem components and carcinogenic in nature. The removal of reactive azo dye Remazol Brilliant Orange 3RID (RBO3RID) and anthraquinone dye Reactive Blue MR (RBMR) by nanoscale zero-valent iron (NZVI) particles was investigated in this study. The dyes were

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degraded up to 97% by NZVI particles under different experimental conditions like NZVI dosages (0.15–0.3 g/L), initial dye concentrations (100–500 mg/L), and pH values (2–12). NZVI was found to work the best in the pH range of 8–12 which is the typical range of pH in textile wastewater. One gram of NZVI could remove up to 2757 mg of RBO3RID dye and 2207 mg of RBMR dye, and more than 80% dye removal was achieved within the first 15 minutes of reaction. FT-IR analyses showed the end products after the degradation are amines.

1. Introduction

Dyes used in textile industries find their way to the environment via wastewater. The textile industry utilizes many dyes and new dyes have been developed for better fixation onto the fabrics (Kasiri and Safapour, 2014; Lewis, 2014; Holme, 2002). More than 100,000 types of synthetic commercial dyes (∼700,000 tons) are used in the world every year (Basturk and Karatas, 2015). Up to 15% of the dyes finds its way to the wastewater streams (Basturk and Karatas, 2015). Being chemically very reactive, the dyes are harmful to the ecosystem components at macro and molecular levels (Leme et al., 2015) and are known carcinogens (Alves de Lima et al., 2007). Further, degradation products from dyes may be toxic to aquatic life and even carcinogenic to human (Gao et al., 2010). Most textile dyes are known for their photo and heat stability and do not degrade easily in the environment (Basturk and Karatas, 2015).

The textile wastewaters from the cotton mill are characterized by high chemical oxygen demand (COD) (650–2100 mg/L) and low 5-day biochemical oxygen demand (BOD_5) with low BOD/COD ratio (∼0.10) (Sun et al., 2015) and, as such, is not easily biodegradable. Wool and cotton fabric dying units may have even higher COD values (∼7900 and ∼1100–4600 mg/L, respectively) (Bisschops and Spanjers, 2003).

During the past years, many physicochemical processes for the treatment of dye-containing wastewaters have been reported. Electrocoagulation is one of the main processes being promoted for textile dye removal (Kobya et al., 2014) but it is chemical and energy intensive and produces a significant amount of toxic sludge. Adsorption is also not an effective and attractive mechanism for dye removal even with innovative adsorption medium (Gao et al., 2010, 2015). Membrane filtration is highly effective but generates highly toxic concentrates and is cost prohibitive and may foul membranes easily (Chidambaram et al., 2015). Pazdzior et al. (2009) proposed an integrated process where concentrate from the membrane process was treated biologically (90% removal of color). Advanced oxidation processes that use ozonation (Panda and Mathews, 2014), ultra-violet/hydrogen-per-oxide (Basturk and Karatas, 2015), and Fenton oxidation (Soares et al., 2015) are also effective in dye removal, but they are not economical and easy to use in most cases. On the other hands, biodegradation of dye is a challenge not only because of the low BOD/COD ratio but also the presence of metals, metalloids, salts, and other toxicants (Imran et al., 2015). Conventional and innovative biological processes have been tried including adsorbent assisted biodegradation using sequencing batch reactor (SRB) (Santos and Boaventura, 2015), aerobic–anaerobic bacteria (Popli and Patel, 2015), and packed bed reactor using a consortium of bacteria (Patel and Gupte, 2015). While biological processes work to certain extent and they are difficult to be sustained in textile wastewater.

Azo dyes are a group of popular dyes used in textile industries, and their removal from wastewater has been extensively studied (Popli and Patel, 2015). Anthraquinone dyes are the new group very popular dyes in the industry because of their bright color, high fixation rate, and strong color fastness (Basturk and Karatas, 2015). However, as discussed earlier, there are no established and accepted technology for textile dye treatment and most of the methods are either very slow or technology intensive. Given the limitations of the current technologies there is a need to develop efficient technologies for textile effluent treatment with specific emphasis on dyes. Azo dyes are extensively studied and literature data can be used to compare new technologies with the current ones. On the other hand limited studies have been conducted on the degradation of anthraquinone dyes.

Zero-valent iron (ZVI) has been reported to decolorize azo dye solution via reduction of the azo bond ($N{=}N$) through surface mediated reaction (Phukan et al., 2015). The cleavage of the azo bond ($N{=}N$) in the chromophore of an azo dye leads to decolorization of the dye solution. ZVI was also used to degrade anthraquinone dyes (He et al., 2012). He et al. (2012) concluded that chromophores of dyes were destroyed during the decolorization process along with the transformation of amino and aromatic rings.

Nanotechnology is an emerging area and has been used for textile dye removal with varying degree of success. Abbasi and Asl (2008) reported the TiO_2 nanoparticle use for Basic Blue 41 degradation and Das et al. (2014) used Pd nanoparticles for the removal of Azo dyes. However, these and other recent work need additional chemical addition (e.g., H_2O_2, borohydride) and/or energy (e.g., sonication, UV radiation). There are also concerns about the fate and transport of the nanomaterials used. Nanoscale zero-valent iron (NZVI) has been used by authors for environmental contaminant remediation because it is relatively non-toxic to the ecosystem components (Almeelbi and Bezbaruah, 2012; Krajangpan et al., 2012; Bezbaruah et al., 2011). NZVI has been used for the removal of various textile dyes. Azo dyes like Acid Blue A, Methyl Orange, Sunset Yellow