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

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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 3R (RBO3R) and anthraquinone dye Reactive Blue MR (RBM) by nanoscale zero-valent iron (NZVI) particles was investigated in this study. The dyes were 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 RBO3R dye and 2207 mg of RBM 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.

Key Words

Nanoparticles; Wastewater; Nanoscale zero-valent iron; reactive textile dye; Reactive Blue MR; Remazol Brilliant Orange 3R; textile effluent

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 find their 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 (BOD₅) with low BOD/COD ratio (~0.10) (Sun and Sun, 2015) and, as such, is not easily biodegradable. Wool and cotton fabric dyeing 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 (Koby 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; Gao et al., 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. (2015) 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 hand, biodegradation of dye is a challenge not only because of the low BOD/COD ratio but also the presence of metals,

30 metalloids, salts, and other toxicants (Imran et al., 2015). Conventional and innovative biological
31 processes have been tried including adsorbent assisted biodegradation using sequencing batch
32 reactor (SRB)(Santos and Boaventura, 2015), aerobic-anaerobic bacteria (Popli and Patel, 2015),
33 and packed bed reactor using a consortium of bacteria (Patel and Gupte, 2015). While biological
34 processes work to certain extent and they are difficult to be sustained in textile wastewater.

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

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

51   Nanotechnology is an emerging area and has been used for textile dye removal with
52 varying degree of success. Abbasi et al. (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 (Rahman et al. 2014), Reactive Yellow K-RN (Mao et al. 2015), Acid Blue 113 (Shu et al. 2016), Reactive Black 5, Reactive Red 198, and Blue Black R were treated NZVI and with Pd and TiO_2 nanoparticles (Satapanajaru et al., 2011). Azo dye Congo Red treatment with NZVI was reported and the end products were demineralized with added Fenton reaction (Shih and Tso, 2012). Compared to azo dyes research, anthraquinone dye degradation with NZVI is not extensively tried. In the recent years Cheng et al. (2015) have studied degradation of an anthraquinone dye (Reactive blue 19) with CMC embedded NZVI. He et al. (2012) has done a comparative degradation study for azo, anthraquinone and triphenylmethane dyes. NZVI has much higher surface area ($25\text{-}52\text{ m}^2/\text{g}$) compared to microscale ZVI ($1\text{-}2\text{ m}^2/\text{g}$) (Thompson et al., 2010). The dye removal mechanism being surface area mediated, it is expected that higher dye removal will be achieved with NZVI than with non-nano ZVI. This study uses NZVI for the degradation of azo and anthraquinone dyes in oxic conditions and under the influence of different operational parameters (e.g., reaction time, initial dye concentration, and pH). The degradation byproducts are analyzed using FT-IR and the mechanisms of dye removal by the nanoparticles are elucidated.

2. Experimental Section

2.1. Chemicals

Two reactive dyes were used in this study (**Table 1**). Other chemicals were received from various suppliers. The dyes and other chemicals were used in the experiments as received unless otherwise specified.

2.2 Synthesis of NZVI

NZVI particles were synthesized by following the method developed by Krajangpan et al., 2012, and this method is modified for increasing the stability of the NZVI. This synthesis is a bottom up approach using ethanol water system without maintaining the inert conditions (Wang et al., 2006, Yuvakkumar et al., 2011). Ethanol was chosen because of its hygroscopic nature and its higher dissolved oxygen solubility, so addition of ethanol causes a reduction in oxidation of the nanoparticles by forming a protective layer on the outer sphere of the nanoparticles. Moreover, other researches already established that ethanol can serve both as solvent and reducing agent (Pal et al., 2009). Reduction of ethanol is two-step process, in the 1st step acetaldehyde forms and in the second step it further reduced to acetic acid. It is also noted that the intermediate acetaldehyde is less stable, and is stronger reductant than ethanol (Wang 2013). Though reduction potential of ethanol water system is not enough for reduction of Fe^{3+} to Fe^0 ($E_0 = -0.04\text{V}$ vs SHE), it can maintain effective reducing environment to prevent further oxidation of Fe^0 in open air (Yuvakkumar et al., 2011).

2.3 Experimental:

Each dye (1 g) was separately dissolved in 1L of distilled water to prepare 1000 mg/L stock solutions. Stock dye solutions were diluted to prepare working solutions with desired concentrations (100-500 mg/L). Borosilicate glass bottles (100 mL) fitted with rubber septum were used as the reactors. Dye solutions (100 mL) and NZVI (0.15-0.3 g/L) were added to each reactor prior to pH adjustment ($\text{pH} = 2-11$). The contents in the reactors were briefly sonicated in an ultrasonic bath to ensure proper dispersion of the nanoparticles. The reactors were rotated in a shaker to reduce mass transfer resistance on the nanoparticle surface. Sacrificial reactors (in triplicate) were withdrawn at specific time intervals (2, 4, 6, 8, 10, 15 and 20 min) and allowed to sit for a brief period before withdrawing samples. The samples were filtered and the filtered samples were stored in a refrigerator and analyzed within 24 h. Controls were run with only dye (no NZVI) and samples collected, prepared, and stored the same way (as samples with NZVI) for analysis.

2.4 Analysis and characterization:

The dye concentration was measured using a UV-VIS spectrophotometer (1601SHIMADZU) at 492 nm and 596 nm wavelengths for RBO3RID dye and RBMR dye, respectively. Calibration was done before and after each day's measurements and the average values were used to plot the calibration curve. The calibration curve was used to determine dye concentrations in samples. The pH and oxidation reduction potential (ORP) values were monitored simultaneously. The ORP values are corrected for pH and reported in mV with reference to hydrogen electrode (E_h) at pH 7.00. The Fourier transform infrared spectra of the dyes and degraded products were recorded on a Thermo Nicolet iS10 spectrometer using KBr pellets in the range $4000-400\text{ cm}^{-1}$. X-ray

diffraction (XRD) was done a Panalytical X'Pert Diffractometer, in the scan range of 35–100° 2θ with a scan speed of 1.2° min⁻¹. Micrographs of NZVI particles were taken using a high resolution transmission electron microscope (HRTEM, Technai TF20 ST) operated at 200 KV. Prior to the grid preparation for TEM analysis the sample was dispersed in ethanol for 8 h, and then 2-3 drops of the NZVI in ethanol solution were placed onto a copper grid. The samples were then put in a vacuum hood till the ethanol was evaporated completely and were analyzed using the TEM.

3. Results and discussion

3.1 Characterization:

The synthesized iron nanoparticles were spherical in shape (**Fig.1a**). The particle diameter was found to be <35 nm (**Fig.1b**) with an average diameter of 16.46±5.98 nm (n = 116). The TEM image shows that most particles formed aggregates. XRD plot shows a peak at 45° (a smaller peaks at 64° and at 82°) representing the presence of Fe⁰ in the NZVI particles (**Fig.1c**). Small amounts of oxides can also be seen. Others, however, reported ~16% oxide presence based on Energy-dispersive X-ray spectroscopy even though they found no oxide peak with XRD (Krajangpan et al., 2012).

3.2. Effects of reaction time:

For a 50 mg/L initial dye concentration of both RBO3RID and RBMR dye, a removal efficiency of ~79% was observed after the first 2 min and 98% within 15 min with 0.2 g/L NZVI dose. Only marginal removal was observed beyond 15 min of reaction time. Absorbance peaks of these

dye solutions in the visible region (400-700 nm) disappeared after treatment with NZVI (**Fig. 2a-b**). In aqueous medium, NZVI particles dissociate into ferrous ions ($\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 + \text{OH}^-$), thereby releasing two electrons. The released electrons can rapidly combine with certain organic compounds present in the medium, resulting in reduction of the organic compound. NZVI is known to breakdown the dye via reductive degradation (Cao et al., 1999) and in the present case the azo group in the dye molecule is reduced. With the same NZVI dose (0.2 g/L) the profile of dye concentration reduction versus time for various dye concentrations (**Fig.3a-b**) indicate that same pattern of degradation (very rapid initially and then slower) was achieved irrespective of dye concentration. The decreasing absorbance peak at the λ_{max} (**Fig.2a-b**) indicated that chromophore group was broken down. Azo bond (N=N) was reported to be degraded by zero valent iron in Acid Orange 2(Cao et al., 1999), Reactive Black 8 (Feng et al., 2000), Acid Blue 113 (Nam and Tratnyek, 2012), Acid Red 14 and 18 (Samarghandi et al., 2012), Reactive Black 5, and Reactive Red 198 (Satapanajaru et al., 2011). The absorbance peak from the azo group was reduced in UV/VIS chromatograph after treatment by NZVI indicating degradation of the dye (**Fig.2a-b**).

3.3. Effects of initial dye concentration and NZVI dose:

Dye removal efficiency varied with the initial dye concentration (100 to 500 mg/L) and NZVI dose (0.15 to 0.30 g/L) (**Fig.4a-b**). For 0.15 gNZVI/L dose, the removal efficiency decreased from 96 to 73% for RBO3RID dye (**Fig.4a**) and from 97 to 66% for RBMR dye (**Fig. 4b**) when initial dye concentration was increased from 100 to 500 mg/L. The decrease in removal was modest (only 2.29%) for RBO3RID dye with 0.20 g NZVI/L dose while the decrease was still very prominent with RBMR dye (~20%) when the dye concentration was changed from 100 to

500 mg/L. For 0.25 and 0.30 g NZVI/L, there was marginal (0.07- 0.1%) decrease in removal efficiency for RBO3RID dye with increase in dye concentration. The removal efficiency decrease was marginal (1.3%) for RBMR dye with 0.30 g NZVI/L.

3.4. Unit Removal Capacity (URC):

Unit removal capacity (URC) is calculated based on the removed amount of dyes per unit weight of NZVI particles. Each gram of NZVI particles removed 634, 1261, 1864, 2466 and 2757 mg RBO3RID dye and 645, 1215, 1594, 2045 and 2207 mg RBMR dye when the initial dye concentrations were 100, 200, 300, 400 and 500 mg/L, respectively (**Fig. 4a and 4b**). The higher NZVI doses achieved higher dye removals. However, they had lower URCs at the same initial dye concentration. Above NZVI dosage of 0.25 g/L, the URC values reach saturation (**Fig. 4a and 4b**). Increasing the NZVI dosage beyond this value has little effect on URC. These observations show that the URC increases with increasing dye concentration and proves that NZVI a potential reactive media for dye removal.

3.5. pH and ORP Changes:

Oxidation–reduction potential and pH were monitored during the batch studies with 50 mg/L dye concentration and 0.2 g/L NZVI. During the study, ORP (E_h) dropped (Fig. 5) from initial +418 to - 220 mV quickly (within 3.5 min), and then there was a slower decrease to - 349 mV in about 30 min. ORP increased to - 208 mV in ~90 min. Reductive conditions were attained within 1 min of starting the experiment and continued till much beyond the dye degradation study period (90 min) used in this work. Within the NZVI reaction system there are several factors which play roles in lowering the ORP value. Along with consumption of reducible contaminant and

consequent removal of oxygen, generation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ species and H_2 evolution are the main reason for the drop in ORP (Shi et al. 2011). Major pH variation was also detected during the reaction. pH increased sharply from initial 2.5 to 8.0 within the first 8 min, and then remained more or less constant till the end of the observation (90 min, pH = 8.1). The pH increase was because of hydroxyl ions generation during NZVI's reaction with water ($\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^-$) (Shu et al., 2010).

3.6. Effects of pH

pH plays an important role in dye removal by zero-valent iron. Here in this study, pH was adjusted adding NaOH solution (1.0 N) or HCl (1.0 N) to change the pH of the solution. While maximum RBO3RID dye removal (94-98%) was achieved in the pH range of 3-9 (**Fig. 6a**), the removal efficiencies significantly dropped at low (pH 2, 62%) and high pH (pH 10-13, 44-49%). The efficiencies of RBMR dye removal (**Fig. 6b**) at lower (pH 2, 61%) and higher pH (pH 12-13, 55-61%) got equally affected while dye removal efficiencies remained high for in the pH range of 3-11 (86-97%). Low decolorization of the test solution was observed in alkaline pH. Oxidized iron (corrosion products) on the surface of the NZVI particles gave a reddish color to the solution. The hydroxides generated also occupy the reactive sites on the NZVI surface and hinder the (dye degradation) reaction (Shu et al., 2007). The corrosion products are also known to cause mass transport limitations from NZVI surface to the active core (Fe^0) of the particles. Ferrous ions dissolve out from the iron surface (Eq. 2 and 3) and combine with hydroxyl ions present in the reaction medium to form ferrous hydroxide, and the hydroxide is precipitated on the iron NZVI surface blocking the reactive sites (Shu et al., 2009). The moderately low pH helps in removing the passivating layer of iron oxides from the NZVI surface (Almeelbi and

Bezbaruah, 2012; Shu et al., 2010) and, thus, exposing the core Fe^0 to react with the dyes. The charge on the surface also changes from positive to negative with an increase in solution pH (Almeelbi and Bezbaruah, 2012; Satapanajaru et al., 2011).

This means that acidic conditions favours reduction process. Low pH range may remove the passivating layers off the NZVI core (Shu et al., 2009; Satapanjaru et al., 2008), rendering the nanoparticles free to react with the azo group in the dye molecules. This result may also be ascribed to the pH_{zpc} (zero point charge) of NZVI. Li et al. (2007) indicated that the pH_{zpc} of NZVI is around 8. At a low pH (pH_{zpc}) the NZVI surface has positive charge, and the dye molecules, with a negative charge bearing SO_3^- group (Fan et al., 2009), attract the NZVI particles towards themselves. Thus, the degradation reaction between the dye molecules and NZVI could be achieved easily. On the other hand, at an alkaline pH, the zero valent iron surface might be covered by corrosion products formed under these conditions. This phenomenon causes a lowering of the reducing power of NZVI and mass transport limitations on NZVI surface. The charge of the surface also changes from positive to negative with an increase in solution pH (Stumm et al., 1990). Moreover, in an extremely acidic (pH 2) condition, poor dye removal efficiency was observed possibly because the NZVI particles were dissolved quickly in the bulk solution resulting in a poor reaction media.

The dye degradation data obtained from the pH studies were analyzed for reaction order and rate determination. The data were fitted into zero-, first-, and second-order reactions and it was found that (pseudo) first reaction best describes the degradation reactions. For RBO3RID dye the degradation reaction rate constant (k) varied from 0.0104-0.3556 min^{-1} in the pH range 2-13 with the highest k at pH 5 and the k value was between 0.0820-0.4730 min^{-1} for RBMR dye with the highest k at pH 7 (see **Table S1** and **Table S2** in Supporting Information). The lowest k values for both the dyes were observed at pH 13.

3.7. Confirmation of dye degradation via FTIR spectroscopic Analyses:

FT-IR analyses were done for both of the dyes and their degradation products. The degradation products of the dyes were separated based on their solubility in water and methanol and characterized using FT-IR (**Fig. S1** and **Fig. S2**, Supporting Information).

3.7.1 RBO3RID dye and its degraded products:

During FT-IR analysis of untreated RBO3RID dye (**Fig. 7a**), stretchings were observed at 3422 cm^{-1} (ν_{OH}), 3273 cm^{-1} (ν_{NH}), 2850 cm^{-1} (ν_{CH}), 1671 cm^{-1} (ν_{CO}), 1498 cm^{-1} (ν_{NN}), and 1040 cm^{-1} (ν_{SO}). After reaction with NZVI for 60 min the treated dye did not display stretching at 1498 cm^{-1} (ν_{NN}) but new stretchings appeared at 3366 cm^{-1} (**Fig. 7b**) and 3350 cm^{-1} (**Fig. 7c**) for corresponding primary amines which corroborates that breaking the N=N bond during the treatment with NZVI had taken place indicating cleavage of azo bond present in the parent dye during the treatment with NZVI.

3.7.2 RBMR dye and its degradation products:

When analyzing RBMR dye before treatment, the stretchings were observed at 3421 cm^{-1} (ν_{OH}), 3288 cm^{-1} (ν_{NH}), 2950 cm^{-1} (ν_{CH}), 1718 cm^{-1} (ν_{CO}), 1040 cm^{-1} (ν_{SO}), and 1067 cm^{-1} (ν_{SO}) (**Fig. 8a**). After treating the dye with NZVI for 60 min, water and methanol soluble part (**Fig. 8b**) of degradation products displayed stretching at 1718 cm^{-1} (ν_{CO}), 3381 cm^{-1} , and 3239 cm^{-1} (ν_{NH}) whereas water insoluble degraded products (**Fig. 8c**) displayed stretchings at 3372 cm^{-1} , and 3231 cm^{-1} (ν_{NH}). FTIR of water soluble but methanol insoluble fraction (**Fig. 8d**) did not display any stretches of amine. These data corroborates that the fraction (**Fig. 8d**) did not contain any amine group but other 2 parts (**Fig. 8b-c**) were primary amine compounds which might be only

possible by the breaking of C-N bond from central benzene ring due to stabilization of benzoin free radical. This was confirmed when methanol and water soluble part(**Fig. 8d**) displayed stretching at 3448 cm^{-1} (ν_{OH})and 1130 cm^{-1} , 1110 cm^{-1} (ν_{SO}).It may be inferred that the selected dye had undergone degradation in such a way that it ruptured its extended conjugation destroying the chromophore.

4. Conclusions

In this study, efficient RBO3RID and RBMR dye degradation in aqueous solution was achieved with nanoscale zero valent iron (NZVI) particles. The efficiency of dye removal depended on NZVI dosage, initial dye concentration, and pH of the solution. RBO3RID and RBMR dye removal was negatively affected in extremely basic (pH 12-13) or acidic conditions (pH 2). Irrespective of dye concentration or NZVI dosage, the most part of the degradation reaction occurred within the first 15 min. Highest unit removal capacities (URCs) of RBO3RID and RBMR dye were observed to be 2756.7 and 2207.33 mg dye/g NZVI, respectively, when dye concentration varied between 100 and 500 mg/L. The FT-IR spectra showed that both azo dye and anthraquinone degradation products were always the corresponding amines. For the anthraquinone dye, the end products were also found to be the corresponding amines. Based on the observations in this study, it may be concluded that nanoscale zero-valent iron (NZVI) can be a viable alternative for dye removal from textile mill wastewater.

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Table 1. Details of the two commercial dyes used in this study

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Figure 1. Characteristics of freshly produced nanoscale zero-valent iron (NZVI) particles used in this study: (a) Transmission electron microscope (TEM) monograph of NZVI particles; (b) Particle size distribution of NZVI counted from TEM monographs. The average diameter was 16.46 ± 5.98 nm ($n = 116$); and (c) X-ray Diffraction (XRD) spectra of the particles. **Prominent peaks of Fe^0 were observed.**

Figure 2. Absorption spectra of dye during reaction at different time interval (0 to 30 min): (a) RBO3RID dye; and (b) RBMR dye.

Figure 3. Residual dye concentration over time for various initial dye concentrations during treatment with NZVI: (a) RBO3RID dye; and (b) RBMR dye. NZVI concentration was 0.2 g/L mg/L and pH was not adjusted. The vertical error bars are $\pm$ standard deviations. The data points are joined by straight lines for ease of reading only and do not represent trendlines.

Figure 4. Dye removal efficiency of NZVI for different initial concentrations of (a) RBO3RID dye, and (b) RBMR dye. The vertical error bars are $\pm$ standard deviations. The data points are joined by straight lines for ease of reading only and do not represent trendlines.

Figure 5. Change of pH and oxidation reduction potential (ORD) of RBO3RID dye solution (50 mg/L over time in the presence of 0.2 g/L of NZVI. The ORP values were corrected for pH and expressed as mV with standard hydrogen electrode at pH 7. ORP values indicate that the reaction took place under reduction conditions. Other dye showed similar pattern (data not shown).

Figure 6. Effect of pH on dye removal efficiency of NZVI (a) RBO3RID dye, and (b) RBMR dye. NZVI concentration was 0.2 g/L and pH was not adjusted. The vertical error bars are $\pm$ standard deviations. The data points are joined by straight lines for ease of reading only and do not represent trendlines.

Figure 7. FT-IR spectra of RBO3RID dye and before and after treatment with NZVI (0.2 g/L and pH was not adjusted): (a) Pure RBO3RID dye, (b) Water insoluble degradation by-products, and (c) Water soluble degradation by-products.

Figure 8. FT-IR spectra of RBMR dye and before and after treatment with NZVI (0.2 g/L and pH was not adjusted): (a) Pure RBMR dye, (b) Water soluble and methanol soluble degradation by-products, (c) Water insoluble and methanol soluble degradation by-products (d) Water soluble degradation by-products.

Table 1. Details of the two commercial dyes used in this study

Details	Remazol Brilliant Orange 3RID(RBO 3RID)	Reactive Blue MR(RBMR)
Molecular Formula	C ₂₀ H ₁₇ N ₃ Na ₂ O ₁₁ S ₃	C ₂₃ H ₁₂ Cl ₂ N ₆ Na ₂ O ₈ S ₂
Molecular Weight	617.54	681.39
Chemical structure		
Maximum absorbance ($\lambda_{\max}$)	492 nm	596 nm
C.I. No	17757	61205
CAS No.	2225-83-1	13324-20-4/4499-01-8
Supplier	Colour Chem, Mumbai, India	Colour Chem, Mumbai, India

Figure 1.

Figure 1.

(a)

(b)

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Graphical Abstract