



## Kinetics of zero-valent iron reductive transformation of the anthraquinone dye Reactive Blue 4

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### ABSTRACT

The effect of operational conditions and initial dye concentration on the reductive transformation (decolorization) of the textile dye Reactive Blue 4 (RB4) using zero-valent iron (ZVI) filings was evaluated in batch assays. The decolorization rate increased with decreasing pH and increasing temperature, mixing intensity, and addition of salt ( $100 \text{ g L}^{-1}$  NaCl) and base ( $3 \text{ g L}^{-1}$   $\text{Na}_2\text{CO}_3$  and  $1 \text{ g L}^{-1}$  NaOH), conditions typical of textile reactive dye baths. ZVI RB4 decolorization kinetics at a single initial dye concentration were evaluated using a pseudo first-order model. Under dye bath conditions and at an initial RB4 concentration of  $1000 \text{ mg L}^{-1}$ , the pseudo first-order rate constant ( $k_{\text{obs}}$ ) was  $0.029 \pm 0.006 \text{ h}^{-1}$ , corresponding to a half-life of 24.2 h and a ZVI surface area-normalized rate constant ( $k_{\text{SA}}$ ) of  $2.9 \times 10^{-4} \text{ L m}^{-2} \text{ h}^{-1}$ . However, as the initial dye concentration increased, the  $k_{\text{obs}}$  decreased, suggesting saturation of ZVI surface reactive sites. Non-linear regression of initial decolorization rate values as a function of initial dye concentration, based on a reactive sites saturation model, resulted in a maximum decolorization rate ( $V_m$ ) of  $720 \pm 88 \text{ mg L}^{-1} \text{ h}^{-1}$  and a half-saturation constant ( $K$ ) of  $1299 \pm 273 \text{ mg L}^{-1}$ . Decolorization of RB4 via a reductive transformation, which was essentially irreversible (2–5% re-oxidation), is believed to be the dominant decolorization mechanism. However, some degree of RB4 irreversible sorption cannot be completely discounted. The results of this study show that ZVI treatment is a promising technology for the decolorization of commercial, anthraquinone-bearing, spent reactive dye baths.

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### 1. Introduction

Reactive dyes are extensively used in the textile industry to dye mainly cotton, as well as wool and polyamide fibers because of their wide variety of color shades, high wet fastness profiles, ease of application and brilliant colors. Reactive dyeing is typically performed at 30–85 °C in dye baths which contain 25–100  $\text{g L}^{-1}$  salt (NaCl or  $\text{Na}_2\text{SO}_4$ ), and 2–50  $\text{g L}^{-1}$   $\text{Na}_2\text{CO}_3$  (or a combination of  $\text{Na}_2\text{CO}_3$  and NaOH) [1]. Under typical reactive dyeing conditions, up to 50% of the initial dye remains in the spent dye bath in its hydrolyzed form, which has no affinity for the fabric, resulting in colored effluent [1]. In addition to the presence of dye, high salt concentrations and high pH values further complicate the treatment of spent reactive dye baths [2,3]. Although azo dyes represent about 60% of all reactive dyes used by the textile industry, other classes of reactive dyes, such as anthraquinone and to a lesser degree phthalocyanine dyes, are extensively used either as primary or secondary

dyes in commercial di- and trichromatic dyeing formulations [1,4]. Most studies dealing with the decolorization of textile wastewater have been conducted with azo dyes. Relatively fewer studies have been conducted with anthraquinone dyes. Therefore, effective and efficient decolorization processes for reactive anthraquinone dyes need to be developed.

Many decolorization processes have been applied, but not all processes work well for all colored wastewaters [5]. Physical processes, such as membrane separation, removed up to 99% of a variety of reactive dyes in laboratory studies [6] and were successful in a pilot scale study [7]. However, most physical processes are typically used at low flow rates due to cost, membrane fouling and flux decline, and the resulting high-salt content concentrate requires further treatment [5,8]. Conventional aerobic biological treatment processes are ineffective against dyes [3,5,9]. The major color removal mechanism is adsorption to the solids, but reactive dyes adsorb poorly due to their high aqueous solubility. Anaerobic biological processes have the capacity to reductively decolorize dyes, but anthraquinone dyes are inhibitory to methanogenic systems [10].

Among chemical dye decolorization processes, reduction and Fenton processes are the most widely used. Use of zero-valent iron (ZVI) for dye decolorization is growing because of its abundance,

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low toxicity, low cost and effectiveness as a reducing agent. ZVI reductive transformation is believed to be surface-mediated and is coupled with the oxidation/corrosion of ZVI to  $\text{Fe}^{2+}$ , while two electrons are released. The reduction mechanism involves several steps: diffusion to metal surface, adsorption to the metal surface, transfer of electrons from the metal surface to the adsorbed contaminant resulting in chemical reduction, desorption of product(s), and diffusion of product(s) to the bulk solution [11]. Recent studies have reported that contaminants are reduced by adsorbed atomic hydrogen (nascent hydrogen) and not by direct transfer of electrons from the ZVI surface [12,13].

This work is part of a broader project on the development of closed-loop, in-plant decolorization systems to economically renovate and reuse spent textile reactive dyebaths. The objective of the work presented here was to assess the effect of key parameters on the kinetics of the ZVI reductive transformation of Reactive Blue 4 (RB4), a commercially important anthraquinone dye. Further kinetic analysis, characterization of dye products resulting from the reductive transformation of RB4, as well as a proposed reaction pathway will be reported in a subsequent communication. To the best of our knowledge, this is the first report on the use of ZVI for the decolorization of an anthraquinone dye.

## 2. Materials and methods

### 2.1. Dye

Commercial RB4 (Procion Blue MX-R; Color Index 61205) was obtained from DyStar LP, Charlotte, NC, USA and used without any further purification. The molecular structure of unreacted RB4 (dichlorotriazinyl reactive group), as well as RB4 characterization data and property values have been previously reported [14]. Preparation of reacted (i.e., hydrolyzed) dye solutions was based on the simulation of typical textile dyebath conditions as follows. Aliquots of 5.0 g dye were dissolved in 50 mM NaOH solution (resulting pH  $11.6 \pm 0.1$ ), heated to and kept at  $85^\circ\text{C}$  for 1 h and then diluted to 1 L after cooling while adjusting the pH to 7.0 with 1N HCl.

### 2.2. Iron

ZVI was obtained from two sources: Fisher Scientific (filings, 40 mesh, cat. no. I57-500), and Connelly-GPM Inc. (filings,  $-8+20$  mesh). Fisher Scientific iron filings were sieved to obtain the 14–35-mesh (1.4–0.5 mm) size fraction, which was rinsed with deionized water several times until the supernatant was clear. The filings were rinsed with methanol five times, transferred to a bottle and its headspace was purged with helium until the filings were dry. Connelly iron filings were acid treated (0.05 M HCl) in a sonicating bath until the supernatant was clear, transferred to a bottle and rinsed with deionized water and methanol as described above. The bottle was then sealed and its headspace purged with helium. The Fisher Scientific and Connelly iron filings had a specific surface area (BET method) before/after treatment of 1.85/1.77 and 1.80/2.97  $\text{m}^2\text{g}^{-1}$ , respectively. Fisher iron was used for all assays, except for the effect of mixing intensity and the effect of initial RB4 concentration assays.

### 2.3. Batch decolorization assays

Batch assays were conducted to evaluate the effect of the following parameters on the decolorization kinetics of RB4: pH, temperature, mixing intensity, reactive dyebath conditions (i.e., salt and base) and initial dye concentration. For each assay, ZVI ( $55.9\text{gL}^{-1}$ ) was added to triplicate serum bottles or tubes. The bottle/tube was then sealed with a rubber stopper and aluminum

crimp and purged for 10 min with helium. Aliquots of a  $5\text{gL}^{-1}$ , helium pre-purged, RB4 stock (unreacted or reacted) was added to each bottle/tube, along with either DI water or a salt and base solution to arrive at the following initial, liquid concentrations:  $100\text{gL}^{-1}$  NaCl,  $3\text{gL}^{-1}$   $\text{Na}_2\text{CO}_3$  and  $1\text{gL}^{-1}$  NaOH. The pH of the salt and base solutions was adjusted to 7 beforehand. The bottles/tubes were then wrapped in aluminum foil and placed either on an end-over-end tumbler (4 or 7 rpm) or a variable-speed orbital shaker in a  $22^\circ\text{C}$  controlled temperature room, unless otherwise noted. The initial RB4 concentration for all assays was  $300\text{mgL}^{-1}$ , except for the assays which tested the effect of salt and base, as well as the effect of the initial RB4 concentration on the decolorization kinetics. For all assays, iron-free controls were used.

### 2.4. Analytical methods

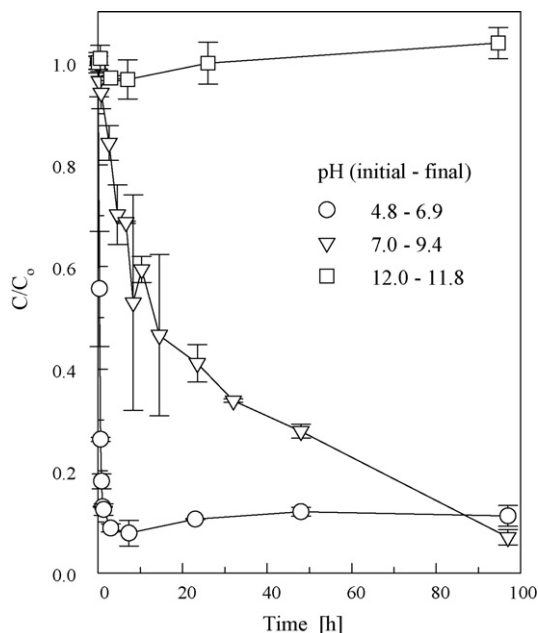
Spectrophotometric analyses were carried out using a UV-visible HP Model 8453 spectrophotometer equipped with a diode array detector (Hewlett Packard, Palo Alto, CA, USA). Samples analyzed with the spectrophotometer were first centrifuged for 5 min at 14,000 rpm in 2 mL polypropylene microcentrifuge tubes and, if necessary, the supernatants were diluted with deionized water. The dye concentration was quantified based on sample absorbance at the maximum dye absorbance wavelength (598 nm) and previously prepared calibration curves.

High performance liquid chromatography (HPLC) analyses were carried out following previously reported procedures [14]. Spectrophotometric absorbance measurements of decolorized RB4 solutions at 598 nm resulted in a low intensity residual color attributed to dye decolorization products. However, HPLC analyses of the same samples revealed the complete disappearance of RB4. Because the spectrophotometric measurements gave results comparable to that of HPLC analyses (e.g., overall decolorization rates), in all experiments reported here, color was routinely followed by spectrophotometric absorbance measurements and HPLC measurements were periodically carried out to confirm such results.

## 3. Results and discussion

### 3.1. Effect of pH

In order to assess the effect of pH on the ZVI RB4 decolorization kinetics, initially organic (HEPES, MOPS, CHES) as well as inorganic (carbonate, phosphate and borate) buffers were considered. However, excessive sorption of RB4 and its decolorization products on the reaction vessels (even on Teflon) was observed in the presence of all organic buffers, which prevented their use. Even though the three inorganic buffers did not cause dye sorption, they were ruled out based on their iron complexation effects. It has been noted that carbonate initially increases the iron corrosion rate, but that over time it passivates the iron surface leading to reduced transformation rates [15]. Stumm et al. [16] and Martini and Muller [17] state that phosphate and borate buffers, respectively, passivate the iron surface. In addition, at low pH values, phosphate increases the iron corrosion rate [16]. Although such an effect could be beneficial, the alkaline conditions of textile dyebaths preclude ZVI dye decolorization at very low pH values. Based on the above and because sorption was not observed in un-buffered assays, it was decided not to use any buffer. Preliminary tests showed that the pH increased by two pH units, at the most, when the starting pH was circumneutral, and that the RB4 decolorization rates for two assays within this pH range were approximately the same (data not shown).



**Fig. 1.** Effect of pH on the ZVI transformation kinetics of reacted RB4 (experimental conditions: RB4 300 mg L<sup>-1</sup> in DI water; mixing with an end-over-end tumbler at 7 rpm; 22 °C) (error bars represent ± one standard deviation of the mean).

The effect of pH on the ZVI RB4 decolorization was assessed at three initial pH values: 4.8, 7 and 12 (Fig. 1). The final pH values for the three initial pH conditions were 6.9, 9.4 and 11.8, respectively. RB4 decolorization did not take place at or above pH 12, because there is minimal corrosion taking place at this pH, and thus there is no source of reducing power. The RB4 decolorization rate increased dramatically at pH values below 9 and was higher at lower pH values (Table 1). The pH of the dye solution appears to have a more significant effect on the decolorization rate than the salt and base concentration (see Section 3.4, below). These results agree with previous reports on the ZVI transformation of dyes [18–23]. The main reasons that transformation rates decrease with increasing pH values are: (a) corrosion rates generally decrease as pH increases; (b) the charge of the iron surface changes from (+) to (-) as the pH increases [16], which diminishes the adsorption of the negatively charged, anionic reactive dyes; (c) due to increased deprotonation of the dye amino bridges, the (-) charge of reactive dyes increases as the pH increases [14], resulting in changes of the dye's redox activity, further increasing the negative effect of the iron surface charge as discussed above [24]; (d) the stability of several dyes (especially anthraquinone reactive dyes with dichlorotriazinyl reactive groups) increases as the pH increases due to intramolecular hydrogen bonding [25].

**Table 1**  
ZVI decolorization kinetics of Reactive Blue 4 as a function of pH<sup>a</sup>

pH <sup>b</sup>	$k_{\text{obs}}$ (h <sup>-1</sup> ) <sup>c</sup>	$r^2$	$t_{1/2,\text{obs}}$ (h)	$k_{\text{SA}}$ (L m <sup>-2</sup> h <sup>-1</sup> ) <sup>d</sup>
4.8–6.9	2.056 ± 0.168	0.975	0.34	2.1 × 10 <sup>-2</sup>
7.0–9.4	0.035 ± 0.004	0.888	19.8	4 × 10 <sup>-4</sup>
12.0–11.8	– <sup>e</sup>	–	–	–

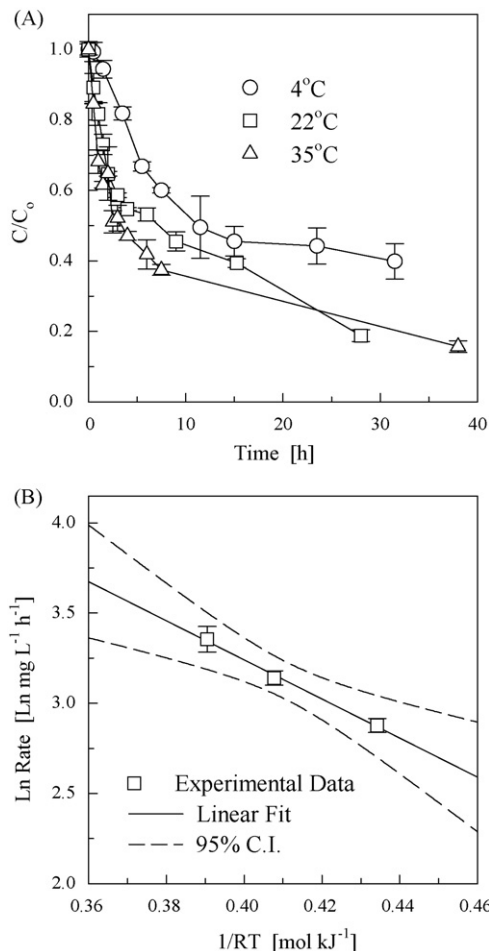
<sup>a</sup> Experimental conditions: RB4 300 mg L<sup>-1</sup> in DI water, 55.9 g L<sup>-1</sup> iron filings (Fisher), mixing with an end-over-end tumbler at 7 rpm, 22 °C.

<sup>b</sup> pH range (initial/final).

<sup>c</sup> Mean ± standard error ( $n \geq 6$ ).

<sup>d</sup>  $k_{\text{SA}} = k_{\text{obs}} / (99.344 \text{ m}^2 \text{ L}^{-1})$ .

<sup>e</sup> Decolorization not observed at this pH range.



**Fig. 2.** Effect of temperature on the ZVI transformation kinetics of reacted RB4. (A) Experimental data. (B) Linear regression according to the Arrhenius equation (see text) (experimental conditions: RB4 300 mg L<sup>-1</sup> in DI water; mixing with an end-over-end tumbler at 7 rpm) (error bars represent ± one standard deviation of the mean).

### 3.2. Effect of temperature

The effect of temperature on the ZVI RB4 decolorization kinetics was evaluated at 4, 22 and 35 °C (Fig. 2A). The pH range was 7.1–8.4, 7.5–8.7 and 7.5–8.9, for the three temperature conditions, respectively. As the temperature increased, the dye transformation rate increased, which is attributed to increased corrosion rates and collisions between the dye and the ZVI surface. The temperature of spent reactive dyebaths is 60 °C or greater. Thus, spent dyebath decolorization at relatively high temperatures not only increases the decolorization rate without significant additional energy input (cost), but also conserves energy if the renovated dyebath is reused in the dyeing operation.

The observed RB4 decolorization rate data were plotted (see Fig. 2B) according to the linearized Arrhenius equation:

$$\ln r = \ln A - E_a \left[ \frac{1}{RT} \right] \quad (1)$$

where  $r$  is the initial RB4 transformation rate (mg L<sup>-1</sup> h<sup>-1</sup>);  $A$  is a frequency factor (mg L<sup>-1</sup> h<sup>-1</sup>);  $E_a$  is the activation energy (kJ mol<sup>-1</sup>);  $R$  is the gas constant (0.008314 kJ mol<sup>-1</sup> K<sup>-1</sup>);  $T$  is the absolute temperature (K). The initial RB4 transformation rates were calculated using data during the first 6 h, thus eliminating the residual color artifact described below. Linear regression per-

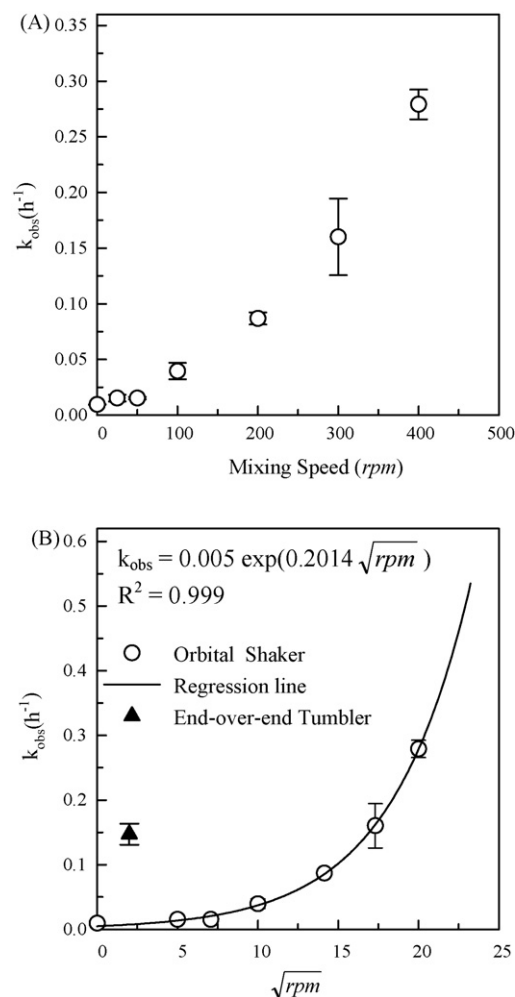
formed based on the data shown in Fig. 2B resulted in the following values (mean estimate  $\pm$  standard error):  $E_a = 10.9 \pm 0.7 \text{ kJ mol}^{-1}$ ,  $A = 1987 \pm 1 \text{ mg L}^{-1} \text{ h}^{-1}$ ;  $r^2 = 0.996$ . The calculated activation energy corresponds to about a 20% increase in the RB4 reduction rate for a  $10^\circ\text{C}$  increase in temperature.

The activation energy reported here is in good agreement with the value of  $11.7 \pm 2.1 \text{ kJ mol}^{-1}$  determined by Lee [26] for the reductive decolorization of RB4 in a continuous-flow fluidized bed reactor system using an anaerobic, halophilic mixed culture. An approximately doubling of the reduction rate of the azo dye Orange G was observed with an increase of temperature from  $22$  to  $35^\circ\text{C}$  of continuous-flow columns containing Master Builders Inc. cast iron filings at an influent dye concentration of  $100 \text{ mg L}^{-1}$  [22]. The calculated apparent activation energy for the Orange G study was equal to  $38.9 \text{ kJ mol}^{-1}$ , which corresponds to an 80% increase in the dye reduction rate for a  $10^\circ\text{C}$  increase in temperature. Thus, a much higher temperature dependence was observed in the Orange G study as compared to the present study. This difference may be due to the type of iron, dye and other experimental conditions used in these two studies. The activation energy value is indicative as to whether the ZVI-mediated process is reaction or mass transfer controlled. Based on previously published activation energy values for ZVI processes, Tratnyek et al. [27] determined that a value of  $25 \text{ kJ mol}^{-1}$  represents a transition between reaction and mass transfer control, whereas a value of  $15 \text{ kJ mol}^{-1}$  and lower represents a process which is entirely mass transfer controlled. Based on the above, the reductive decolorization of RB4 in the present study was mass transfer controlled.

### 3.3. Effect of mixing intensity

Many studies have concluded that ZVI transformation reactions are mass transfer limited [11,18,28,29], while two studies have shown that such transformations were controlled by reaction kinetics [30,31]. Whether or not the process is mass transfer limited will ultimately depend on the contaminant and the operating conditions of the system. A criterion for whether or not the ZVI reductive process is mass transfer limited is the dependence of the reaction rate constant on the mixing intensity [11].

In order to evaluate the effect of mixing intensity on the ZVI RB4 decolorization kinetics, a series of decolorization assays were conducted with an orbital shaker at the following rotational speeds: 0, 4, 25, 50, 100, 200, 300 and 400 rpm. For comparison purposes, one decolorization assay was conducted with an end-over-end tumbler at 4 rpm. The initial pH was 7.3 and the final pH ranged from 8.4 to 9.8. Fig. 3A shows that as the mixing intensity increased, the RB4 decolorization rate increased. However, these data followed a non-linear pattern with respect to the square root of the mixing speed, which is contrary to that observed by several researchers [18,28–30]. The data of the present study are best described by an exponential function as shown in Fig. 3B. Nam and Tratnyek [29] stated that deviation from linearity of the decolorization rate vs. the square root of the mixing speed is likely due to inefficient mixing by the orbital shaker at or below 60 rpm, as well as to the ZVI surface site saturation effect as discussed in a later section. The RB4 decolorization rate using the tumbler at 4 rpm was almost as fast as that obtained with the orbital shaker at 300 rpm, which demonstrates that mixing characteristics are more important than mixing speed. Thus, when comparing transformation rates, caution should be exercised relative to the type of mixing device used. The end-over-end tumbler method of mixing was used for most of the assays conducted in this study because of the increased mass transfer and thus enhanced RB4 transformation rates.



**Fig. 3.** Effect of mixing intensity (rpm) on the ZVI transformation kinetics of reacted RB4. (A) Pseudo first-order decolorization rate constant ( $k_{\text{obs}}$ ) as a function of mixing speed (rpm). (B) Non-linear regression fit of rate constant data as a function of the square root of mixing speed (rpm) (experimental conditions: RB4  $300 \text{ mg L}^{-1}$  in DI water; mixing with an orbital shaker at different rpm; one data point for mixing with end-over-end tumbler at 4 rpm;  $22^\circ\text{C}$ ) (error bars represent  $\pm$  one standard deviation of the mean).

### 3.4. Effect of salt and base

Even though ZVI transformation of RB4 was proven effective in DI water batch systems, it was vital that this technology be tested under actual textile dyebath conditions (i.e., high salt, base and dye concentration). Changes in the ionic strength of the solution may affect the iron corrosion, and thus the RB4 reduction rate. A batch decolorization assay was conducted at an initial RB4 concentration of  $1000 \text{ mg L}^{-1}$  with salt ( $100 \text{ g L}^{-1}$ ), base ( $3 \text{ g L}^{-1} \text{ Na}_2\text{CO}_3$  and  $1 \text{ g L}^{-1} \text{ NaOH}$ ), as well as with salt and base combined and compared to the no salt and base condition. The salt and base addition resulted in the following ionic strength: salt, 1.71 M; base, 0.11 M and salt plus base, 1.82 M.

RB4 decolorization rates were measured based on non-linear regression of the experimental data according to pseudo first-order kinetics and results are shown in Table 2. The presence of both salt and base resulted in the fastest RB4 decolorization kinetics followed by the salt-only, then base-only and finally no salt or base condition. While the addition of base did not have a significant effect on the decolorization rate, in part because of the small amount of base added, addition of salt resulted in a significant increase in the decolorization rate. It can be concluded that an increased ionic strength,

**Table 2**  
ZVI decolorization kinetics of Reactive Blue 4 as a function of salt and base<sup>a</sup>

Condition	pH <sup>d</sup>	$k_{\text{obs}}$ (h <sup>-1</sup> ) <sup>e</sup>	$r^2$	$t_{1/2, \text{obs}}$ (h)	$k_{\text{SA}}$ (L m <sup>-2</sup> h <sup>-1</sup> ) <sup>f</sup>
DI water	7.1–9.3	0.010 ± 0.002	0.960	68.6	1.0 × 10 <sup>-4</sup>
Salt <sup>c</sup>	7.0–9.1	0.023 ± 0.002	0.991	29.6	2.4 × 10 <sup>-4</sup>
Base <sup>b</sup>	8.5–9.1	0.014 ± 0.002	0.974	49.9	1.4 × 10 <sup>-4</sup>
Salt and base	7.7–8.8	0.029 ± 0.006	0.958	24.2	2.9 × 10 <sup>-4</sup>

<sup>a</sup> Experimental conditions: 1000 mg L<sup>-1</sup> reacted RB4, 55.9 g L<sup>-1</sup> iron filings (Fisher), 22 °C and mixing with an end-over-end tumbler at 4 rpm.

<sup>b</sup> Base: 3 g L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> and 1 g L<sup>-1</sup> NaOH.

<sup>c</sup> Salt: 100 g L<sup>-1</sup> NaCl.

<sup>d</sup> pH range (initial/final).

<sup>e</sup> Mean ± standard error ( $n = 6$ ).

<sup>f</sup>  $k_{\text{SA}} = k_{\text{obs}} / (99.344 \text{ m}^2 \text{ L}^{-1})$ .

which is due to both base and salt, resulted in an increased RB4 transformation rate consistent with previously reported results by Johnson et al. [32], but contrary to the results of Reardon [33], Li and Farrell [34] and Alessi and Li [35], who reported that an increase of ionic strength had either no effect or decreased the transformation rates. Such disagreements may be attributed to the fact that different compounds behave differently with increasing ionic strength due to different salts used and differences in intermolecular forces, polarity and size [36]. In the case of RB4, it is possible that a higher degree of dye aggregation took place with increasing ionic strength, which in turn reduced the solubility of the dye and enhanced the overall removal of RB4 under the high salt and base conditions. Enhanced aggregation of reactive dyes with increased concentration of salt and base has been documented [14,37,38]. However, as discussed in Section 3.5, below, RB4 was not recovered at the end of batch decolorization assays when the high ionic strength solutions were replaced with DI water. Therefore, it was confirmed that dye reductive transformation took place as opposed to physical dye removal enhanced by aggregation.

The pseudo first-order rate constant ( $k_{\text{obs}}$ ) and the surface area-normalized rate constant ( $k_{\text{SA}}$ ) data are reported in Table 2. It has been reported, however, that  $k_{\text{SA}}$  values should not be directly compared without first determining if the relationship between  $k_{\text{obs}}$  and the iron mass loading is linear [39]. This observation has significant implications relative to the use of  $k_{\text{SA}}$  values to compare ZVI technologies. More research in this area is necessary to allow accurate rate comparisons under different ZVI experimental conditions and use of such experimental rates in engineering applications.

### 3.5. Effect of initial RB4 concentration

The effect of initial RB4 concentration on its ZVI decolorization kinetics was evaluated at a concentration range from 100

to 1500 mg L<sup>-1</sup> at typical reactive textile dyebath conditions (i.e., 100 g L<sup>-1</sup> NaCl, 3 g L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> and 1 g L<sup>-1</sup> NaOH), using Connolly iron filings. The end-over-end tumbler at 4 rpm was used for this assay, which was carried out at 22 °C. The assay lasted from 47 to 337 h, depending on the initial dye concentration. The pH values increased throughout this assay as shown in Table 3. Decolorization rates were determined based on pseudo first-order kinetics and non-linear regression (Table 3). The highest  $k_{\text{obs}}$  value was  $1.52 \pm 0.21 \text{ h}^{-1}$ , which corresponds to a  $k_{\text{SA}}$  value of  $9.2 \times 10^{-3} \text{ L m}^{-2} \text{ h}^{-1}$ . Reported ZVI decolorization rates for azo dyes are in the range of 3.84–31.8 h<sup>-1</sup>, depending on dye concentration and mixing conditions, with a typical value of 21.0 h<sup>-1</sup>, which corresponded to a  $k_{\text{SA}}$  value of  $12.6 \text{ L m}^{-2} \text{ h}^{-1}$  [29]. Thus, based on the above listed  $k_{\text{SA}}$  values, it appears that the ZVI decolorization rate of the anthraquinone dye RB4 was at least three orders of magnitude lower than the reported rates for azo dyes. However, this comparison of  $k_{\text{SA}}$  values may be inaccurate due to a possible non-linear relationship between  $k_{\text{obs}}$  and the iron mass loading as discussed above. The relationship between the  $k_{\text{obs}}$  value and the initial dye concentration is non-linear (Fig. 4), and is best described by an exponential function, as follows:  $k_{\text{obs}} = 8.7 \exp(-0.175 C^{0.5})$ ,  $r^2 = 0.994$ ; where  $C$  is the initial RB4 concentration (mg L<sup>-1</sup>).

Fig. 5 shows the UV-visible spectra during the ZVI decolorization of RB4 at an initial dye concentration of 1500 mg L<sup>-1</sup>. As the dye decolorization proceeded, the absorbance at 598 nm gradually decreased and the absorbance at 485 nm increased due to the formation of RB4 decolorization products. With prolonged incubation, the absorbance at 485 nm decreased. The residual absorbance at 598 nm was attributed to decolorization products and not to the parent dye, especially after an incubation period of 97 h and was confirmed using HPLC analysis. Additional supporting evidence and a proposed reaction pathway will be reported in a subsequent communication. The RB4 decolorization was the result of a reductive chemical reaction based on the following observations: (a) HPLC analyses revealed large quantities of intermediates and products which were not present in the dye stock solution; (b) the temperature dependence of the decolorization rate and the resulting activation energy support a chemical reaction; (c) at the end of batch decolorization assays when all RB4 was depleted, recovery tests conducted by replacing the assay solutions with DI water several times did not yield any RB4 by HPLC analysis. Under these, low ionic strength conditions, any RB4 aggregated and/or sorbed on the ZVI filings would have been released into the solution. Therefore, as mentioned in Section 3.4, above, reductive transformation of RB4 is believed to be the dominant decolorization mechanism. However, some degree of RB4 irreversible sorption cannot be completely discounted. Re-oxidation tests by exposing solutions with the RB4 decolorization products to air for 24 h showed that the decoloriza-

**Table 3**  
ZVI decolorization kinetics of Reactive Blue 4 as a function of initial dye concentration<sup>a</sup>

Initial dye conc. (mg L <sup>-1</sup> )	pH <sup>b</sup>	$k_{\text{obs}}$ (h <sup>-1</sup> ) <sup>c</sup>	$r^2$	$t_{1/2, \text{obs}}$ (h)	$k_{\text{SA}}$ (L m <sup>-2</sup> h <sup>-1</sup> ) <sup>d</sup>	Initial decolorization rate (mg L <sup>-1</sup> h <sup>-1</sup> ) <sup>e</sup>	$r^2$
100	7.9–8.1	1.520 ± 0.209	0.950	0.45	9.2 × 10 <sup>-3</sup>	80.3 ± 14.8	0.905
300	7.9–8.1	0.397 ± 0.058	0.961	1.75	2.4 × 10 <sup>-3</sup>	135.8 ± 39.0	0.977
500	7.9–8.0	0.145 ± 0.033	0.917	4.78	9.0 × 10 <sup>-4</sup>	190.6 ± 66.1	0.973
700	7.9–8.5	0.160 ± 0.038	0.930	4.33	1.0 × 10 <sup>-3</sup>	246.8 ± 78.2	0.938
1000	7.9–8.5	0.069 ± 0.016	0.922	10.05	4.0 × 10 <sup>-4</sup>	313.0 ± 103.3	0.902
1500	7.8–8.4	0.041 ± 0.008	0.946	16.91	3.0 × 10 <sup>-4</sup>	389.7 ± 105.0	0.824
300 <sup>f</sup>	7.2–9.8	0.147 ± 0.016	0.983	4.72	9.0 × 10 <sup>-4</sup>	72.6 ± 11.4	0.930

<sup>a</sup> Experimental conditions: 55.9 g L<sup>-1</sup> iron filings (Connolly), 100 g L<sup>-1</sup> NaCl, 3 g L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub>, 1 g L<sup>-1</sup> NaOH, mixing with an end-over-end tumbler at 4 rpm.

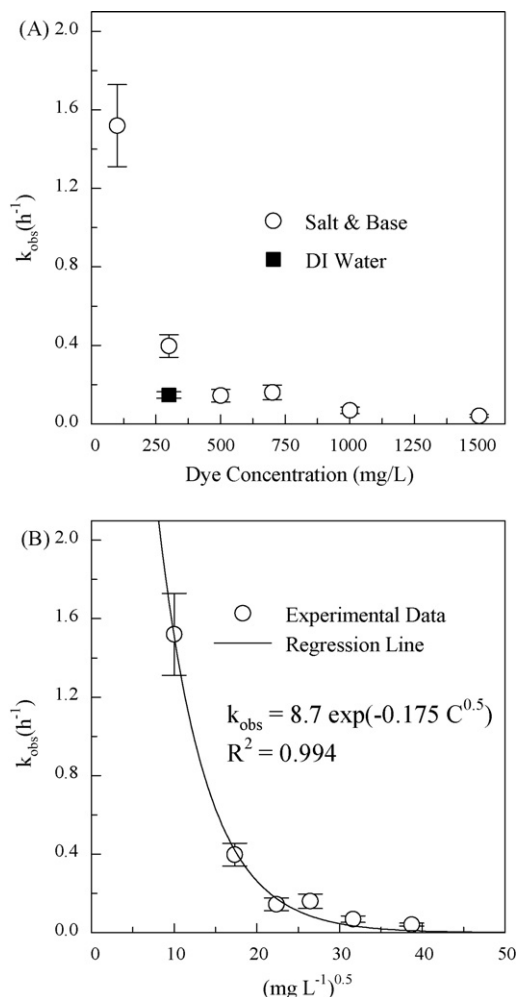
<sup>b</sup> pH range (initial/final).

<sup>c</sup> Mean ± standard error ( $n \geq 6$ ).

<sup>d</sup>  $k_{\text{SA}} = k_{\text{obs}} / (165.84 \text{ m}^2 \text{ L}^{-1})$ .

<sup>e</sup> Mean ± standard error ( $n \geq 3$ ).

<sup>f</sup> Reacted RB4 300 mg L<sup>-1</sup> in DI water, instead of the salt and base solution.



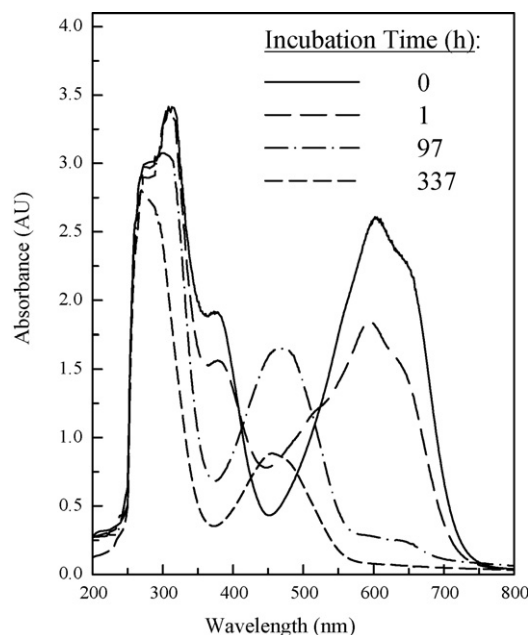
**Fig. 4.** Effect of initial dye concentration on the pseudo first-order rate constant ( $k_{\text{obs}}$ ) for the ZVI RB4 decolorization (experimental conditions:  $100 \text{ g L}^{-1}$  NaCl,  $3 \text{ g L}^{-1}$   $\text{Na}_2\text{CO}_3$  and  $1 \text{ g L}^{-1}$  NaOH, except one data point for an assay conducted in DI water; mixing with end-over-end tumbler at 4 rpm;  $22^\circ\text{C}$ ) (error bars represent  $\pm$  one standard deviation of the mean).

tion was essentially irreversible (2–5% re-oxidation based on an increase of the absorbance at 598 nm).

Several ZVI studies have shown that the reaction rate can shift order depending on the initial contaminant concentration. At relatively high initial contaminant concentrations, saturation of the ZVI surface reactive sites is common in heterogeneous reactions [15,29,40]. The initial volumetric RB4 decolorization rate data ( $r$ ,  $\text{mg L}^{-1} \text{ h}^{-1}$ ) were used to perform a non-linear regression based on the following reactive sites saturation equation [27]:

$$r_0 = -\frac{dC}{dt} = \frac{V_m C_0}{K + C_0} \quad (2)$$

where  $r_0$  is the initial volumetric RB4 decolorization rate ( $\text{mg L}^{-1} \text{ h}^{-1}$ );  $V_m$  is the maximum decolorization rate ( $\text{mg L}^{-1} \text{ h}^{-1}$ );  $C_0$  is the initial dye concentration ( $\text{mg L}^{-1}$ );  $K$  is the half-saturation constant ( $\text{mg L}^{-1}$ ). The  $r_0$  values, calculated for a time period of 2 h, increased monotonically, but non-linearly with increasing initial RB4 concentration (Table 3). Such behavior may be explained by the saturation of ZVI surface reactive sites. Based on the non-linear regression of the experimental data according to Eq. (2), the following values were obtained (mean  $\pm$  standard error):  $K = 1299 \pm 273 \text{ mg L}^{-1}$  and  $V_m = 720 \pm 88 \text{ mg L}^{-1} \text{ h}^{-1}$  ( $r^2 = 0.991$ ;  $n = 7$ ). Based on the reactive sites saturation model, Nam and Trat-



**Fig. 5.** UV-visible spectra during the decolorization of reacted RB4 (experimental conditions: initial RB4 concentration,  $1500 \text{ mg L}^{-1}$ ;  $100 \text{ g L}^{-1}$  NaCl,  $3 \text{ g L}^{-1}$   $\text{Na}_2\text{CO}_3$  and  $1 \text{ g L}^{-1}$  NaOH; mixing with end-over-end tumbler at 4 rpm;  $22^\circ\text{C}$ ).

nyek [29] reported  $K$  and  $V_m$  values equal to  $1017 \text{ mg L}^{-1}$  and  $30,700 \text{ mg L}^{-1} \text{ h}^{-1}$ , respectively, for the ZVI decolorization of the azo dye Crocein Orange G. Based on these results, the  $K$  values for the ZVI decolorization of both azo and anthraquinone dyes are of the same order of magnitude. However, the  $V_m$  for RB4 was more than 40-fold lower than that of the azo dye Crocein Orange G. The value of  $K$  is approximately constant for a particular contaminant, but the value of  $V_m$  varies with both the type/grade of ZVI and the experimental conditions (mixing, temperature, etc.) [29,32].

#### 4. Conclusions

Relatively fast and practically irreversible decolorization of RB4 was achieved with ZVI filings. The decolorization rate increased with decreasing pH and increasing mixing intensity, temperature and ionic strength. The latter two parameters are of particular importance because of the high ionic strength and temperature conditions of typical, reactive textile dyebaths. RB4 decolorization did not take place at a pH value of 12 or above, whereas the decolorization rate increased dramatically at pH values below 9. The effect of both the mixing intensity and the initial dye concentration on the RB4 decolorization rate demonstrate that the ZVI RB4 decolorization achieved in the present study is a surface-catalyzed, mass transfer-limited process.

Overall, the results of this study indicate that ZVI treatment is a promising technology for the decolorization of commercial, anthraquinone-bearing, spent reactive dyebaths, which upon renovation can then be reused in the dyeing process as process water. Such a system has the potential to not only decrease final wastewater volume and treatment cost, but also minimize water and salt use as well as the discharge of textile pollutants such as salt and dyes.

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