Impacts of dyebath auxiliaries on the reductive discoloration of Acid Orange 7 dye by high-carbon iron filings

Raja Kumar and Alok Sinha

ABSTRACT

This study proposed that the physicochemical effects of common dyebath auxiliaries on the bulk dye solution as well as on the iron surface can influence the reductive discoloration of effluent containing Acid Orange 7 (AO7) dye using high-carbon iron filings. Sodium chloride increased the discoloration rate because of the pitting corrosion on the iron surface, triggered by chloride anion. ‘Salting out’ effect of ammonium sulfate improved the reaction rate up to a certain concentration, beyond which it could compete with dye molecules for the reactive sites, as revealed by formed sulfite and sulfide. Urea drastically reduced the discoloration rates by its chaotrope effect on the bulk solution and by wrapping around the iron surface. Organic acids, namely acetic acid and citric acid, stimulated iron corrosion to improve the discoloration rates. The discoloration reaction was biphasic with an initial fast reaction phase, where in every case more than 70% discoloration was observed within 5 min of reaction, preceding a slow reaction phase. The experimental data could be well described using biphasic kinetics equation ($R^2 > 0.997$ in all cases) and a biphasic equation was developed considering the individual impact of co-existing auxiliaries on AO7 discoloration.

Key words | Acid Orange 7 (AO7), biphasic kinetics, discoloration, dyebath auxiliaries, high-carbon iron filings (HCIF)

INTRODUCTION

Effective color fixation is the main goal of dyers. To achieve this goal, the color chemist tries hard to develop an appropriate dyebath solution chemistry that could improve exhaustion of dyes onto the fiber. This is achieved by adding a chemical that could lead to a more uniform dyeing and higher color yield. Hence, large amount of salts are used during exhaust dyeing, and urea in continuous dyeing and printing with water-soluble anionic dyes. For example, sodium chloride is widely added to a dyebath to increase the degree of aggregation of the dye molecules via the common ion effect. It promotes exhaustion of sulfonated dye to the fiber by suppressing its ionization in solution, thus reducing the solubility imparted to it through sulfonate groups. This modifies the solution equilibrium in favor of movement of dye aggregates from the solution to the fiber (Hamlin et al. 1999). In contrast, urea is added in the continuous dyeing and printing to achieve high aqueous dye solubility, which is a prerequisite for successful coloration. These salts pass into the wastewater along with the unixed dye and may influence the treatment process for the discoloration of azo dyes.

Available literature revealed that co-existing organic and inorganic compounds could significantly affect the physico-chemical effluent treatment processes (Liu & Lo 2011). Especially, the surface-mediated discoloration technologies, like zero-valent metals (ZVMs), are most likely to be affected by the presence of these auxiliaries. The reductive cleavage of the azo linkage (−N−N−) of azo dyes by ZVMs requires the dye molecules to reach the reactive sites on the metal surface. Hence, the presence of dyebath auxiliaries might influence the reactivity of ZVMs by affecting their corrosion behavior, by forming precipitate on the metal surface and/or by competing with dye molecules for reduction on the reactive sites on the metal surface.

This paper reports results of a study undertaken on the effect of commonly used dyebath auxiliaries on the
The discoloration of azo dye-containing wastewater by high-carbon iron filings (HCIFs). HCIFs are iron/carbon/silicon alloys (2–4% C; 1–3% Si), in which more carbon is present, which remains embedded as graphite flakes within the metal (Sinha & Bose 2006, 2011, 2014). Although HCIF has proven to be effective in discoloration of azo dyes (Kumar & Sinha 2016), further investigation into the interaction between dyebath auxiliaries and HCIF is important for maximizing the efficiency of this process. This study presents results on the individual effect of dyes (Kumar & Sinha 2014–2015), with the studied concentration also examined. It is expected that this work may provide a new insight into the treatability of dyebath effluent using ZVMs and the results can be extended to design the practical application of HCIF.

**MATERIALS AND METHODS**

**Materials and chemicals**

Commercially available mono-azo dye C.I. Acid Orange 7 (AO7) was purchased from Atul Ltd (India) and was used as received. Analytical grade sodium chloride (NaCl), ammonium sulfate (NH₄)₂SO₄, urea, citric acid and acetic acid were purchased from Merck (India). Deionized (Mill-Q) water was used to make all the solutions. The HCIF prepared by the method discussed previously by Kumar & Sinha (2016) had a Brunauer–Emmett–Teller (N₂) surface area of 1.4 m²/g.

**Experimental methods and analysis**

Time series batch experiments were carried out in 35 mL capacity glass vials with screw caps (Borosil, India). AO7 concentration and HCIF mass were kept constant at 100 mg/L and 28.56 g/L, respectively, for all the experiments and only the concentrations of auxiliaries and acids used were amended according to experimental need. For experiments using NaCl, (NH₄)₂SO₄ and urea, 0.5 M HCl was used to adjust the initial solution pH to 3 while for other experiments it is described specifically. For proper mixing, the vials were placed on a test tube rotator (Rotospin, Tarsons, India) at 30 rpm. The ambient temperature was 25 ± 2 °C for all experiments. Duplicate vials along with a blank were removed from the rotator at specified time interval for sampling and analysis. The supernatant was filtered through GF/C filter paper (1.2 μm nominal pore size, Whatman, Springfield Mill, UK) and was quantified for color using a UV-visible spectrophotometer (UV-1800 series, Shimadzu, Japan) at the λmax of 484 nm specific for AO7 (Kumar & Sinha 2015). In the batch experiments probing the effect of sulfate, the turbidimetric method (Standard Methods 4500 SO₄⁻E) was used for determining sulfate concentration, and the generated sulfide (Standard Methods 4500-S²⁻D) and sulfide (Standard Methods 4500-S²⁻F) were determined by the iodometric method as given in standard methods (APHA 2005). An atomic absorption spectrometry (AAS) (GBC Avanta, GBC Scientific Equipment, USA) was used for determining dissolved iron content.

Fourier transform infrared (FTIR) analysis of urea and used HCIF samples collected after 10 min of reaction was performed using an FTIR spectroscope (Perkin Elmer, Spectrum One, USA). The used HCIF was dried under N₂ atmosphere immediately after sampling to prevent oxidation. Dry HCIF and/or urea were finely ground to powder form with pure KBr (5:95 ratio) (BDH chemicals, UK) and pressed into translucent pellets using a laboratory press applying 40 MPa pressure for 50 sec. FTIR scans of the prepared KBr pellets were carried out at the mid-IR region spanning from 400 cm⁻¹ to 4,000 cm⁻¹ at 16 scan speed.

**Discoloration kinetics analysis**

Very fast AO7 discoloration was observed in the first 5 min after which the discoloration process was very slow. Evidently, the discoloration process was biphasic and, hence, the kinetics was elucidated using the biphasic rate equation (Equation (1)) given below:

\[
C = C_1 e^{-k_1t_1} + C_2 e^{-k_2t_2}
\]

where C is the concentration at time t, C₁ and C₂ are the AO7 concentration at t = 0 min and t = 5 min, respectively; t₁ is the rapid discoloration phase (i.e. first 5 min) and t₂ is the slow discoloration phase (from 5 min to 120 min); k₁ and k₂ are the pseudo-first-order AO7 discoloration rates observed for the first 5 min and after 5 min, respectively, the values of which were determined by non-linear regression of the observed discoloration data.
RESULTS AND DISCUSSION

Effect of sodium chloride

Sodium chloride accelerated AO7 discoloration. The results exhibited in Figure 1(a) and Table 1 reveal an increase in the AO7 discoloration and rate constant with the increase in NaCl concentration from 0 g/L to 6 g/L. The discoloration followed biphasic kinetics with high values of regression coefficient ($R^2 > 0.998$). With NaCl concentration of 6 g/L, highest discoloration efficiency and $k_1$ of 98.41% and $0.869 \text{ min}^{-1}$, respectively, were achieved in the rapid reaction phase. Since the standard reduction potential of Na$^+$ ions (2.71 V) is less than that of Fe$^{2+}$ ions (0.44 V), it could hardly affect the degradation reactivity of HCIF (Efecan et al. 2009) and chloride ion is expected to affect the reactivity of the HCIF surface. The rate enhancing effect of NaCl mainly resulted from three aspects affecting the bulk solution as well as the HCIF surface. First is the ‘salting out’ effect of NaCl that affects the solubility of azo dye. The Na$^+$ ions help to reduce the repulsion between the negative charges on the dye molecules, so that they could get closer and become dye aggregates (Ingamells 1993). Higher degree of dye aggregation reduces the solubility of the dye. The Na$^+$ ions help to reduce the repulsion between the negative charges on the dye molecules, so that they could get closer and become dye aggregates (Ingamells 1993). Higher degree of dye aggregation reduces the solubility of the dye and enhances its partitioning onto the HCIF surface. Secondly, adding NaCl would improve the conductivity of the dye solution. The resultant increase in kinetic energy and molecular motion could accelerate the mass transport rate of both the reactant and products between the solution and solid phases. Thirdly, pitting and crevice corrosion induced by the chloride ion in solution could improve the reactivity or surface area of HCIF (Fan & Wang 2015). The chloride dissolves the oxide layer and induces pits and cracks on the HCIF surface, forming iron chloride, which hydrolyzes to produce iron hydroxide and hydrochloric acid (Su et al. 2012). Thus, an autocatalytic process begins where HCl can further rejuvenate the surface.

Table 1: Biphasic AO7 removal rates in the presence of different salt concentration

<table>
<thead>
<tr>
<th>Dyebath auxiliaries</th>
<th>Concentration (mg/L)</th>
<th>Removal rate (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.641</td>
<td>0.018</td>
</tr>
<tr>
<td>1</td>
<td>0.678</td>
<td>0.020</td>
</tr>
<tr>
<td>2</td>
<td>0.718</td>
<td>0.020</td>
</tr>
<tr>
<td>3</td>
<td>0.764</td>
<td>0.023</td>
</tr>
<tr>
<td>4</td>
<td>0.830</td>
<td>0.023</td>
</tr>
<tr>
<td>5</td>
<td>0.859</td>
<td>0.024</td>
</tr>
<tr>
<td>6</td>
<td>0.869</td>
<td>0.025</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.641</td>
<td>0.018</td>
</tr>
<tr>
<td>100</td>
<td>0.720</td>
<td>0.022</td>
</tr>
<tr>
<td>300</td>
<td>0.765</td>
<td>0.022</td>
</tr>
<tr>
<td>500</td>
<td>0.672</td>
<td>0.021</td>
</tr>
<tr>
<td>1,000</td>
<td>0.640</td>
<td>0.020</td>
</tr>
<tr>
<td>2,000</td>
<td>0.627</td>
<td>0.020</td>
</tr>
<tr>
<td>Urea</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.641</td>
<td>0.018</td>
</tr>
<tr>
<td>10</td>
<td>0.556</td>
<td>0.018</td>
</tr>
<tr>
<td>30</td>
<td>0.489</td>
<td>0.018</td>
</tr>
<tr>
<td>50</td>
<td>0.395</td>
<td>0.013</td>
</tr>
<tr>
<td>75</td>
<td>0.360</td>
<td>0.010</td>
</tr>
<tr>
<td>100</td>
<td>0.340</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Figure 1: (a) Biphasic discoloration of AO7 by HCIF at different NaCl concentrations. Inset figure shows the temporal variation in AO7 concentration after 5 min. (b) Variation in dissolved iron concentration with increase in NaCl concentration.
increase the surface area and generate electrons for the discoloration reaction. Linear increase in the dissolved iron concentration (refer Figure 1(b)) with the increase in NaCl concentration also supports the discussion.

**Effect of sulfate**

Sulfate compounds are commonly used as a promoter and a buffering agent in the dyeing industry. The effect of sulfate in discoloring azo dye was studied using sulfate concentrations ranging from 100 mg/L to 2,000 mg/L in the form of (NH₄)₂SO₄. Results, shown in Figure 2(a) and Table 1, suggest that the presence of (NH₄)₂SO₄ in the wastewater promotes dye discoloration until a certain concentration, beyond which the dye removal efficiency and rate are retarded. In the rapid reaction phase (i.e. in first 5 min), highest AO7 discoloration of 97.20% was observed using 300 mg/L of (NH₄)₂SO₄, and this declined with a further increase in its concentration for reasons discussed later in this section.

(NH₄)₂SO₄ is also a ‘salting out’ agent and may impart a rate enhancing effect similar to NaCl onto the dye molecules in the bulk solution. Moreover, formation of ‘green rust’ during the reaction may also positively impact the reaction rates. ‘Green rust’ appeared shortly after contact of HCIF

![Figure 2](https://iwaponline.com/wst/article-pdf/74/5/1217/459537/wst074051217.pdf)

**Figure 2** | (a) Biphasic discoloration of AO7 by HCIF at different ammonium sulfate concentration. Inset figure shows the temporal variation in AO7 concentration after 5 min. (b) FE-SEM image of greenish suspended particles observed in the experiment. (c) Temporal variation in aqueous sulfate concentration and formation of sulfite and sulfide during AO7 reduction and sulfur (S) mass balance: (i) 2,000 mg/L initial sulfate concentration, (ii) 100 mg/L initial sulfate concentration.
with sulfate-containing solution (Equation (2)) and remained for the entire duration of the experiment, where more reducing potential conditions prevailed. Field emission scanning electron microscopy (FE-SEM) analyses (Figure 2(b)) of the greenish precipitate obtained from the solution matches a typical surface morphology of the smogrenite–pyroaurite class (Choe et al. 2004). Green rust structural units consist of alternating positively charged trioctahedral metal hydroxide sheets and negatively charged interlayers of anions (Taylor 1980). Anions present in the interlayer positions typically are Cl\(^{-}\), CO\(_3\)^{2\,-} or SO\(_4\)^{2\,-}. Because sulfate was the dominant anion present in the solution, the ideal composition of the precipitated green rust is likely Fe\(_{6}\)(OH)\(_{12}\)SO\(_4\).nH\(_2\)O. Green rust does not prevent electron transfer, and may further act as a reducing agent and, therefore, may account for improved discoloration in the presence of sulfate. Several authors have reported contaminant reduction in the presence of green rust (Etique et al. 2014; Jones et al. 2015).

\[
4\text{Fe}^{2+} + 4\text{Fe}^{3+} + \text{SO}_4^{2-} + 12\text{H}_2\text{O} \\
\leftrightarrow \text{Fe}_6(\text{OH})_{12}\text{SO}_4(\text{sulfate green rust}) + 12\text{H}^+ \tag{2}
\]

Higher sulfate concentration retarded the AO7 discoloration efficiency. The possible reason is that HCIF has a positively charged iron oxide surface under the isoelectric point, and anions that have atoms with a lone pair of electrons can adsorb onto the surface of the iron particles through a coordinate bond, forming both outer-sphere and inner-sphere surface complexes (Hug 1997). Therefore, SO\(_4\)^{2\,-} anions could compete with AO7 molecules in occupying the adsorptive and reactive sites on the HCIF surfaces, because they have similar anion structure, thus lowering the discoloration efficiency (Fan et al. 2009).

During AO7 reduction, sulfate may play a double role: besides being the precursor of electron donor sulfide, it may also compete with the dye molecule as an electron acceptor. To confirm this, tests were carried out to quantify the probable formation of sulfite and sulfide. The results, as shown in Figure 2(c), reveal that AO7 reduction and sulfate reduction proceed simultaneously in the presence of HCIF, with both sulfite and sulfide detected in the solution. With an initial sulfate concentration of 2,000 mg/L (see Figure 2(c-ii)), about 23 mg/L of sulfide and 42 mg/L of sulfite were detected after 120 min of AO7 discoloration, whereas with an initial sulfate concentration of 100 mg/L (see Figure 2(c-ii)), sulfate reduction was faster, forming 12.5 mg/L of sulfide and 14 mg/L of sulfite. Slow sulfite and sulfide formation at high sulfate concentration could result from amassing sulfate molecules occupying the reactive sites on the HCIF surface, the resultant reduced surface corrosion and the competition with dye molecules. In batch assays, the sulfide formed, albeit low in concentration, may contribute to increase in the overall rate of dye reduction because of its chemical reactivity. By accounting for the total sulfur (S), remarkably good mass balance (>95%) was obtained for this experiment. To our knowledge, this is the first ever report on abiomic sulfite and sulfide formation by the reduction of sulfate by any ZVM.

Comparatively, the enhancement in discoloration was less pronounced in the case of sulfate relative to chloride. This could be because the critical stability constants for soluble aqueous complexes between Fe\(^{2+}/\text{Fe}^{3+}\) and inorganic ligands increase with the order: chloride < sulfate (Table 2). Our study shows that the sequence for the azo dye reduction rate for the inorganic ligands is the reverse of the sequence for the strength or affinity of the surface complexation of these inorganic ligands with iron oxides. This could be because formation of sulfate complexes could decrease the number of adsorptive and reactive sites on the iron surface. In the past, sulfate anions have been shown to lower the removal kinetics of both arsenate and arsenite by Peerless Fe\(^{0}\) relative to chloride (Su & Puls 2001).

### Effect of urea

Urea is used in the dyebath to enhance the solubility of the dye, thus leading to a more uniform dyeing and increased color yield. Urea is a hydrophobic agent that acts as an amphiphilic bridge between the solubilized dye and the aqueous media (Shore 1990), thus increasing the aqueous solubility of dyes. The effect of urea in AO7 discoloration was studied at urea concentrations ranging from 10 mg/L to 100 mg/L. The results, displayed in Figure 3(a) and Table 1, show retarded discoloration with increasing urea concentration. This negative effect is attributable to the dual effect of urea, in the bulk phase as well as on the HCIF surface.

In the bulk phase, urea modifies the chemical properties of dye solution, which impairs partitioning of dye molecules onto the HCIF surface. The chaotropic effect of urea in

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Equilibrium</th>
<th>Fe(^{2+}) (aq.)</th>
<th>Fe(^{3+}) (aq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>ML/M.L</td>
<td>–0.2 (I = 0)</td>
<td>0.6 (I = 1.0)</td>
</tr>
<tr>
<td>Sulfate</td>
<td>ML/M.L</td>
<td>2.39 (I = 0)</td>
<td>1.96 (I = 1.0)</td>
</tr>
</tbody>
</table>
aqueous solution weakens the hydrophobic effect of dye molecules, reduces their degree of aggregation (converse effect to NaCl) and increases the number of monomeric species (Hamlin et al. 1999), thus increasing the aqueous solubility of dye molecules. Also, direct interaction of urea with the solute (dye) is also reported to contribute to their solvation in water (Breslow & Guo 1990). Das et al. (2003) reported that the ‘salting in’ effect of urea modifies the interaction between water and organic molecules such that the free energy of adsorption increases. Consequently, the dye molecules become more stable in bulk water, and their partitioning onto the HCIF surface reduces. Another reason for the reduced rates could be decline in solution conductivity in the presence of urea (from 469 μS of initial AO7 aqueous solution to 322 μS of AO7–urea aqueous solution), which reduces electron transport in the AO7–HCIF reaction.

An important reason for the negative effect of urea on the discoloration reaction could be wrapping of the HCIF surface by urea. Urea displays a directional network morphology in aqueous solution by self-association (Zhang et al. 2005). This network forms an even coating on the surface of HCIF, thus creating a steric hindrance effect that makes the reactive sites inaccessible for the dye molecules and inhibits the mass transfer process. The results of AAS analysis of reaction solution, taken after 120 min of reaction, show decrease in dissolved iron concentration from 722 mg/L iron at 0 mg/L urea to 432 mg/L iron at 100 mg/L urea concentration. This also confirms reduced iron corrosion with the increase in urea concentration because of a wrapping film formed around the HCIF surface.

Further investigation on the interaction of urea, AO7 and HCIF was carried out using FTIR as shown in Figure 3(b). Pure urea (refer Figure 3(b-i)) shows vibration bands νC=O at 1,667 cm⁻¹, δNH₂ bending vibration at 1,626 cm⁻¹ and νC=N at 1,455 cm⁻¹, which exhibited a right shift to 1,664 cm⁻¹, 1,624 cm⁻¹ and 1,452 cm⁻¹, respectively, after adsorption to HCIF. This suggests interaction between HCIF surface and urea (O-Fe and N-Fe). Figure 3(b-ii) shows the spectrum of AO7 adsorbed onto HCIF. This spectrum shows an intense band at 1,514 cm⁻¹ attributable to the –N==N– bond vibrations. The bands at 1,037 and 1,121 cm⁻¹ are ascribed to coupling between benzene mode and νs(SO₃) (Stylidi et al. 2003). Bands at 1,182 cm⁻¹ and 1,408 cm⁻¹ are for S–O and –S=O– stretching vibrations of the sulfonate groups; and the bands at 2,925 and 2,854 cm⁻¹ are ascribed to the C–H stretching vibration of AO7. Comparing Figure 3(b-iii) and 3(b-iv) reveals lesser adsorption of AO7 onto the HCIF surface in the presence of urea as indicated by the lower intensity of AO7 characteristic bands. In addition, the weak bands at 751 cm⁻¹ and 1,020 cm⁻¹ in Figure 3(b-iii), attributable to the δ-OH and γ-OH bending vibrations of some lepidocrocite (γ-FeOOH) on the HCIF surface, were absent in Figure 3(b-iv) suggesting reduced corrosion of HCIF surface because of its filming by urea.

**Effect of acetic acid**

Effect of acetic acid (CH₃COOH) on azo dye discoloration was studied at solution pH 2, 3, 4 and 5, and the results are shown in Figure 4 and Table 3. AO7 discoloration efficiency enhanced with the increase in acetic acid concentration; so, the highest discoloration rate was recorded at pH 2. Research conducted in the past has revealed that acetic acid can induce pitting corrosion of tin (Hassan & Fahmy 2008). Pitting corrosion of the HCIF
The anodic reaction that occurs simultaneously at the HCIF surface, in order to balance the charge, is the dissolution of iron (Equation (4)):

$$\text{Fe(s) } \leftrightarrow \text{Fe}^{2+} (\text{aq}) + 2e^-$$  

(4)

Furthermore, during the reaction course, excessive H$_2$ gas bubbles were produced at pH 2 and 3 (Equation (3)). Depending on the surface condition of HCIF, this H$_2$ gas could function as an inhibitor (Zhang et al. 2012) or a reducing agent (Siantar et al. 1996), where the latter effect could help enhance AO7 reduction.

**Effect of citric acid**

Effect of citric acid [(CH$_2$)$_2$COH(COOH)$_3$] on AO7 discoloration studied at solution pH 2, 3, 4 and 5 shows results similar to that in acetic acid/HCIF systems (see Figure 5 and Table 3). The AO7 discoloration reaction, in the presence of citric acid may proceed with the following reactions:

$$\text{Fe}^{2+} + \text{H}_2\text{Cit}^- \rightarrow \text{FeCit} + 2\text{H}^+$$  

(5)

$$\text{FeCit} + \text{H}^+ \rightarrow \text{FeHCit}$$  

(6)

$$\text{FeHCit} + \text{H}_2\text{O} \rightarrow \text{FeO} + \text{H}_2\text{Cit}^- + 2e^- + \text{H}^+$$  

(7)

Here also, a mild evolution of hydrogen bubbles was observed at pH 2 and pH 3 possibly due to reduction of surface can be a potential reason for improved discoloration and is supported well by the dissolved iron concentration profile, which shows a higher concentration of 859 ± 25 mg/L iron in the pH 2 batch reactors compared to the control (581 ± 18 mg/L iron) and the other pH systems. Dissolution of HCIF in acetic acid (HAc) is enhanced by direct reduction of acetic acid on the HCIF surface according to the reaction below (Equation (3)):

$$2\text{HAc} + 2e^- \leftrightarrow \text{H}_2(\text{g}) + 2\text{Ac}^-$$  

(3)

![Figure 4](https://iwaponline.com/wst/article-pdf/74/5/1217/459537/wst074051217.pdf)  
**Figure 4** | Biphasic discoloration of AO7 by HCIF using acetic acid at different pH. Inset figure shows the temporal variation in AO7 concentration after 5 min (AA: acetic acid).

![Figure 5](https://iwaponline.com/wst/article-pdf/74/5/1217/459537/wst074051217.pdf)  
**Figure 5** | Biphasic discoloration of AO7 by HCIF using citric acid (CA) at different pH. Inset figure shows the temporal variation in AO7 concentration after 5 min.

<table>
<thead>
<tr>
<th>Dyebath auxiliaries</th>
<th>Solution pH/Experimental set</th>
<th>Removal rate (min⁻¹)</th>
<th>Initial</th>
<th>After 5 min</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>Not adjusted (pH 5.39)</td>
<td>0.411 0.026 0.999</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH 2</td>
<td>0.618 0.040 1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH 3</td>
<td>0.581 0.037 1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH 4</td>
<td>0.542 0.037 0.999</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH 5</td>
<td>0.533 0.032 0.998</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Citric acid</td>
<td>Not adjusted (pH 5.39)</td>
<td>0.411 0.026 0.998</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH 2</td>
<td>0.579 0.038 0.999</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH 3</td>
<td>0.554 0.035 0.999</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH 4</td>
<td>0.544 0.035 0.997</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH 5</td>
<td>0.497 0.027 0.997</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimental combination</td>
<td>A</td>
<td>0.423 0.025 0.999</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.444 0.032 0.999</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.396 0.025 0.998</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>0.808 0.019 1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
hydrogen ions. These hydrogen bubbles can cause convection in the system, which allows proper mixing and may promote the removal of citrate complexes from the reactive sites on the HCIF surface as well, thus improving dye discoloration (Nishide & Shoda 2012). Also, it was reported that the oxide film in citric acid solution was thin and conductive for electron transfer (Abdel Rehim et al. 2003); therefore the metal oxide film in citric acid was not so influential as to disturb dissolution of HCIF and its reactivity. Further, the dissolved iron concentration increased with decrease in initial solution pH with the highest concentration of 811 ± 42 mg/L recorded at pH 2. It reveals that HCIF surface corrosion was not inhibited by citrate formation, supporting the claim discussed above. Compared to the acetic acid/HCIF systems the dissolved iron concentration was lower in the citric acid/HCIF systems possibly because of the less corrosive nature of citric acid, which resulted in lower discoloration rates in citric acid/HCIF systems.

Effect of various dyebath combinations

Four different sets of experiments were carried out to test the efficiency of HCIF for discoloration of AO7 in the presence of all the salts studied at their highest concentration (i.e. 6 g/L NaCl, 2,000 mg/L (NH4)2SO4 and 100 mg/L urea). The experimental sets were: A (without any salt and acid; initial pH 5.59), B (with all salts and no acid; initial pH 6.56), C (all salts; initial pH adjusted to pH 9 using 1 M NaOH) and D (all salts; initial pH of the solution adjusted to 2 using 1:1 mixture of citric acid and acetic acid). The discoloration profile of AO7 in various combinations is shown in Figure 6 and the rates are shown in Table 3. In set D, AO7 was rapidly removed from solution: 97.83% of the initial AO7 disappeared after 5 min and complete removal was observed within 90 min. Highest dye removal (i.e. 100%) was observed in set D whereas lowest (i.e. 99.50%) was observed in set C. The effect of aggressive reaction boosters like Cl− anion is greatly masked at alkaline pH 9 suggesting that the solution pH may play a dominant role in the reductive dye discoloration process. However, more than 95% final discoloration efficiency achieved in all the studies points towards the remarkable potential of HCIF in treating azo dye-containing textile effluents having vivid solution chemistry.

In the experimental combination sets A, B, C and D, the overall discoloration kinetics is governed by the individual effect of each dyebath auxiliary present in the synthetic wastewater. A biphasic equation was developed taking into account the individual effects (positive or negative) of each dyebath auxiliary on the kinetics of dye discoloration. In such case, the discoloration rate represents the sum of the effect of each dyebath auxiliary present in the wastewater on the kinetics, and hence the proposed equations are as follows.

For the rapid phase (t₁) of AO7 discoloration:

\[ C_A = C_1 e^{-\left(\Delta k_{1NaCl} + \Delta k_{1(NH4)2SO4} + \Delta k_{1Urea} + \left(\Delta k_{1Acetic\ acid} + \Delta k_{1Citric\ acid}\right)/2\right)t_1} \]  

(8)

For the slow phase (t₂) of AO7 discoloration:

\[ C_B = C_2 e^{-\left(\Delta k_{2NaCl} + \Delta k_{2(NH4)2SO4} + \Delta k_{2Urea} + \left(\Delta k_{2Acetic\ acid} + \Delta k_{2Citric\ acid}\right)/2\right)t_2} \]  

(9)

where \( C_A \) and \( C_B \) are the variation in AO7 concentration with time \( t_1 \) and \( t_2 \), respectively; \( C_1 \) and \( C_2 \) are the respective AO7 concentration at \( t = 0 \) min and \( t = 5 \) min; \( k_1 \) and \( k_2 \) are AO7 discoloration rates without any auxiliary for respective discoloration phases; \( \Delta k_{1NaCl}, \Delta k_{1(NH4)2SO4}, \Delta k_{1Urea}, \Delta k_{1Acetic\ acid} \) and \( \Delta k_{1Citric\ acid} \) for the first phase of discoloration and \( \Delta k_{2NaCl}, \Delta k_{2(NH4)2SO4}, \Delta k_{2Urea}, \Delta k_{2Acetic\ acid} \) and \( \Delta k_{2Citric\ acid} \) for the second discoloration phase are the difference in the rate constants when NaCl, (NH4)2SO4, urea, acetic acid and citric acid, respectively, were present at their highest concentration to that obtained in the absence of these auxiliaries. Since, in the experimental combination, acetic acid and citric acid were used in 1:1 ratio to adjust the solution pH, their individual rates were reduced to half. The biphasic equation, thus developed, was fitted for the experimental data obtained with various experimental combinations using dyebath...
auxiliaries (Figure 6). The data of experimental set D simulated well this biphasic equation.

**CONCLUSIONS**

The HCIF-mediated reductive discoloration of azo dye AO7 at varied concentration of commonly used dyebath auxiliaries was investigated. Presence of NaCl causes ‘salting out’ effect in the bulk solution and increases solution conductivity whereas the chloride anion induces pitting corrosion of the HCIF surface. These chemical effects lead to improved discoloration rate with increase in NaCl concentration. (NH₄)₂SO₄ improved the AO7 discoloration efficiency by HCIF at low concentration by virtue of its ‘salting out’ effect on the bulk solution and due to the reducing effect of ‘sulfate green rust’. However, beyond 300 mg/L (NH₄)₂SO₄ concentration, SO₄²⁻ anion could compete with dye molecules in occupying the adsorptive and reactive sites on the HCIF surface, thus inhibiting the reaction. The AO7 discoloration rate reduced drastically in the presence of urea, because of its chaotropic effect on the bulk dye solution and because of it wrapping around the HCIF surface, as revealed by FTIR analysis. Increase in acetic acid and citric acid concentration enhanced the HCIF surface corrosion, thus increasing its reactivity. The discoloration reaction is greatly promoted at pH 2 (in the presence of all the auxiliaries) while at pH 9 the discoloration is retarded. The results reveal that the dye-bath effluent composition influences the reactivity of HCIF, with the solution pH playing a dominant role.

The discoloration reaction followed biphasic reaction kinetics showing an initial rapid discoloration phase preceding a slow phase. Non-linear regression of the experimental data using the biphasic rate equation showed high values of regression coefficients (R² > 0.997) in all the cases. A biphasic equation was developed for AO7 discoloration in the presence of all the auxiliaries by taking into account the individual effect of each auxiliary on discoloration. The data obtained from this biphasic equation simulation fitted well with the data of experimental set D. It is expected that the results of this study may provide a new insight into designing of an effective reduction-based treatment system for textile effluents containing azo dyes.

**ACKNOWLEDGEMENTS**

The authors heartily acknowledge Technical Education Quality Improvement Program Phase II (TEQIP II), ISM, Dhanbad, for providing all necessary assistance for completion of this research work.

**REFERENCES**


Fan, J. H. & Wang, H. W. 2015 Effects of operational parameters and common ions on the reduction of 2,4-dinitrotoluene by scrap copper-modified cast iron. Environmental Science and Pollution Research 22 (13), 9932–9942.


Kumar, R. & Sinha, A. 2016 Reductive transformation and enhancement in biodegradability of mono-azo dye by high carbon iron filings (HCIF). *Desalination and Water Treatment* 57 (7), 3205–3217.


Martel, A. E., Smith, R. M. & Motekaitis, R. J. 2005 NIST Critically Selected Stability Constants of Metal Complexes Database, NIST Standard Reference Database 46, Version 7, NIST, Gaithersburg, MD, USA.


First received 25 January 2016; accepted in revised form 7 June 2016. Available online 23 June 2016