HETEROGENEOUS SOLAR PHOTO-FENTON DEGRADATION OF REACTIVE BLACK 5 USING FOUNDRY SAND AND FLY ASH: VALUE ADDITION TO WASTE

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Abstract. This work evaluates the scope of alternative sources of iron i.e. Foundry Sand (FS), Fly Ash (FA) and mixture of FS and FA in heterogeneous photo-Fenton process for the degradation and decolourization of the dye Reactive Black 5 (RB5). SEM-EDS characterization of FS and FA confirmed the presence of iron and aluminium which are required for photo-Fenton. In case of FS as an iron source, results confirmed the degradation and decolourization efficiency of 90% in 70 min and 45 min respectively when the reaction parameters were H$_2$O$_2$ = 2.2 mM, FS dose = 0.5 g, pH 3. With FA 90% degradation was achieved within 30 min and 93% decolourization rate within 15 min. When a mixture of FS (0.1 gm) and FA (0.05 gm) is used as source of iron 99% degradation and decolourization of the dye was achieved under the reaction conditions where H$_2$O$_2$ = 2.2 mM, FA:FS = 1:2, pH 3.

Keywords: foundry sand; fly ash; dye Reactive Black 5; photo-Fenton; degradation; decolourization.

Introduction

Dye effluents from textile industries are significant sources of environmental pollution as it is among one of the most water demanding sectors (Chaco et al. 2006; Wang et al. 2008). This water consumption, allied to high dosage of dyes, originates extremely colored effluents. Release of these wastewaters to natural environment is described as very problematic to aquatic life as transmission of light, photosynthesis and aquatic life diversity will be affected and is also mutagenic to humans (Chung et al. 1992; Chung, Stevens 1993). The dyes do not bind to the fabric completely and its loss in wastewaters depending on the class of the dye can vary from 2% for the basic dyes to 50% for the reactive dyes, causing serious environmental problems (Park, Choi 2003; Mass, Chaudhari 2005; Pandey et al. 2007). They have high solubility and stability, stability, due to which are widely used in many applications (Mahmoodi, Arami 2009). Reactive Black 5 (RB5) is one of the oldest reactive dyes, which is consumed very heavily in textile industries worldwide for the dyeing of woollen, cotton and nylon fabrics (Arslan et al. 1999). It is reported to be toxic and can cause allergic reactions of the respiratory tract (Lars, Mallika 1997). A variety of physical and chemical processes, such as elimination by adsorption on activated carbon, ozone oxidation, coagulation by a chemical agent, electrochemical method, hypochlorite oxidation etc. are available for the treatment of dye waste effluents (Yoshida et al. 1999; Tanaka et al. 2000). Nevertheless, these methods are usually inefficient, costly, non-destructive and resulted in the production of secondary waste products (Sun et al. 2008). On the other hand, biological treatment usually takes long time besides producing a large quantity of sludge.

Advanced oxidation technologies (AOTs) are innovative methods and are extremely useful where substances are resistant to conventional treatment technologies. AOTs are oxidation processes, where hydroxyl radicals (•OH) generates that are very effective in degrading organic pollutants due to their strong oxidant power and non selective species (Toor et al. 2006). Among these AOTs, Fenton’s reagent is particularly gained attention because of its low cost, the lack of toxicity of the reagents, and absence of a mass transfer limitation due to its simplicity of the technology and homogeneous catalytic nature (Liao et al. 2009). However, it should be pointed out that the homogeneous Fenton process has significant disadvantage of
sludge-containing Fe ion at the end of the wastewater and its removal/treatment is very expensive and needs large amount of chemicals and manpower.

Various waste materials of different kinds have been tested as an iron source in heterogeneous photo-Fenton degradation (Lucking et al. 1998; Chaudhuri, Sur 2000; Mecozzi et al. 2006). Photo-Fenton activity in each of the above case can be related to the activation of hydrogen peroxide (H$_2$O$_2$) by the ions of iron leached from the waste materials into the solution. Iron ions release is slow in the case of heterogeneous photo-Fenton reactions, which limits undesired reaction in comparison with the conventional homogenous catalysis.

To overcome the disadvantages of the homogeneous Fenton process, and also considering the possibility of recovering catalyst, attempt has been made to use foundry sand (FS) and fly ash (FA) as an alternative iron source. The key motivating factor for using FS and FA is to identify its iron leaching potential for photo-Fenton studies along with reuse opportunities. Thus, the study proposes alternatives to landfill disposal and ultimately cost saving for materials that can be reused beneficially.

In this context, the present study investigates the degradation of RB5 using FS, FA and their mixture as a new low-cost iron source for the heterogeneous photo-Fenton process. To the best of our knowledge, this is the first reported study towards the use of foundry sand and fly ash as a heterogeneous catalyst in photo-Fenton degradation of dyes. This would be of economic interest keeping in mind the high costs required for disposal of FS and FA which we are using as a catalyst that is commonly considered as a waste.

1. Experimental

1.1. Reagents and chemicals

Reactive Black 5 (RB5), technical grade (55%), was purchased from Sigma- Aldrich and used as such without any further purification. Waste FS was received from Munjal Industries, Gurgaon (India) and FA was received from thermal plant, Ropar, Punjab (India) as a gift sample and used as received without any further modifications. H$_2$O$_2$ (30% w/v) was obtained from SD Fine Chemicals Limited, India. The pH of the solution was adjusted using 0.1 M H$_2$SO$_4$. Throughout the study, all the chemicals were of analytical grade and used as such without any further purification. For experimental study, 100 mgL$^{-1}$ RB5 solution was prepared and double distilled water was used for the preparation of all solutions.

1.2. Photoreactor and experimental procedure

The shallow pond batch slurry reactor used in this study (Fig. 1) was made up of borosil glass, 160 mm in diameter and 52 mm in height having a capacity of 1200 mL. For heterogeneous solar photo-Fenton studies, 200 ml of RB5 solution (100 mgL$^{-1}$) was taken in this batch reactor at pH 3 and known amount of Fenton reagent (FS+H$_2$O$_2$), (FA+H$_2$O$_2$) and (FS+FA+H$_2$O$_2$) were added. The suspensions were kept in dark under stirring for 30 min for attaining any adsorption-desorption equilibrium between FS, FA and dye. For photo-Fenton studies, the above samples were kept in sunlight under same conditions of stirring and aeration. Samples were taken after regular intervals of time, filtered and analyzed for decolourization and degradation studies using an UV-visible spectrophotometer.

All the reported solar experiments were carried during timings 11.00 a.m. – 3.00 p.m. in months of March-May, 2014 at Patiala, Punjab. To check the reproducibility of results, experiments were repeated thrice and average values are reported with standard deviation varying from 1–3%.

1.3. Analytical analysis

The decolourization and degradation studies were performed with UV-visible (Hitachi V- 500 UV/VIS (Japan)) double- beam spectrophotometer with RB5 at 310 nm and 595 nm.

For the characterization of FS and FA, scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) was performed as shown in Figure 2(a) and (b), Figure 3(a) and 3(b) respectively. Chemical composition of foundry sand and fly ash is reported in Table 1 and Table 2 (with accuracy of ± 0.5–1.0%). The analysis indicated the absence of any heavy metal in FS and FA, thus eliminated any risk of their leaching. A considerable amount of iron (23.16%) in FS and aluminium (17.66%) in FA was reported which could be utilized in photo-Fenton process. Although amount of iron detected in FA was less as compared to FS, but the presence of considerable amount of aluminium confirmed its participation in photo-Fenton reactions which could be used in the place of iron.
2. Results and discussion

2.1 Photo-Fenton studies using foundry sand as an iron source

2.1.1 Preliminary experiments

Preliminary experiments were performed to assess the catalytic activity of FS as a catalyst and the effect of individual parameter in the degradation of RB5 by heterogeneous photo-Fenton process. Low and negligible degradation and decolourization (less than 20%) in 120 min was achieved in the presence of H2O2 only, FS only and sunlight only as shown in Figure 4(a) and 4(b). This could be ascribed to limited production of OH radicals due to the insufficient availability of the resources in all three above cases required for the photo-Fenton process. In Fenton process (H2O2 + FS), 35% degradation in 90 min and 50% decolourization rates in 60 min were achieved. It is worth noting that 75% degradation in 90 min and decolourization efficiency of 85% in 60 min was achieved in the presence of FS as a heterogeneous catalyst, H2O2 and sunlight. The photo-Fenton results indicated that catalyst reacts with H2O2 in the presence of photons to generate OH radicals for the degradation of RB5. In the present work, generation of OH radicals for degradation of RB5 was proposed via photo-Fenton mechanism using FS and FA as an iron source.

![Fig. 2. a) SEM micrograph, b) EDS pattern of FS](image)

![Fig. 3. a) SEM micrograph, b) EDS pattern of FA](image)

<table>
<thead>
<tr>
<th>Table 1. Composition of FS</th>
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<td>Weight %</td>
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<td>Atomic %</td>
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<th>Table 2. Composition of fly ash</th>
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2.1.2. Effect of variation of FS

FS was used as an iron source in varying concentrations ranging from 0.1–1.0 gm during the photo-Fenton treatment process while maintaining the other parameters constant. The results indicated that initial increase of FS till 0.5 gm increases degradation and decolourization of the dye as shown in Figure 5(a). The lower degradation capacity of FS at small concentrations was probably due to the low OH radical production and their availability for oxidation. Further increase of FS dosage from 0.5 gm–1.0 gm, degradation and decolourization of dye decreased. This reduction can be explained by OH radicals scavenging either by the reaction with hydrogen peroxide or by the reaction with Fe$^{2+}$ as expressed in the equations (Djeffal et al. 2013):

$$\text{H}_2\text{O}_2 + \text{OH}^• \rightarrow \text{H}_2\text{O} + \text{OH}_2^•$$

$$\text{Fe}^{+2} + \text{OH}^• \rightarrow \text{OH}^• + \text{Fe}^{+3}$$

The effective degradation (90%) within 90 min and decolourization (90%) within 60 min was achieved at 0.5 gm FS dosage.

2.1.3. Effect of H$_2$O$_2$ concentration

Figure 5(b) shows the degradation and decolourization of RB5 at different dosage of H$_2$O$_2$. To optimize the dosage, H$_2$O$_2$ was varied from 0.0–8.82 mM of the dye solution at fixed FS and pH. Dye removal increases with the increasing dosage of H$_2$O$_2$ till 2.2 mM, after that percentage of removal decreases with further increase in dosage.
becomes constant till 6.61 mM and then decreases with the increasing dosage of \( \text{H}_2\text{O}_2 \). This decrease is due to the fact of scavenging of \( \text{OH}^- \) by \( \text{H}_2\text{O}_2 \) (Walling 1975; Madhavan et al. 2010), can be expressed by the equation:

\[
\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \\
\text{HO}_2^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}_2
\]

Effective degradation (90%) was achieved within 70 min while decolourization (90%) of dye solution was achieved within 45 min of reaction at optimum dose 2.2 mM of \( \text{H}_2\text{O}_2 \).

2.1.4. Effect of pH

The effect of pH on RB5 degradation and decolourization is shown in Figure 6(a) and 6(b). The pH of the reaction was varied from 2–7. 90% degradation and decolourization efficiency was achieved at pH 3, for the reaction time of 70 min and 45 min respectively. At pH 2, nearly similar results were observed. Further increment in the pH from 3 leads to reduction in the degradation (18%) and decolourization (28%) efficiencies. This behaviour could be explained by the formation of ferric hydroxo complexes during the reaction, which blocks the decomposition of hydrogen peroxide catalyzed by the ferrous irons (Faust, Hoigne 1990; Kitis, Kalpana 2007).

2.2. Photo-Fenton studies using FA as an iron source

2.2.1. Preliminary experiment

The similar preliminary studies were performed with FA using different conditions as in the case of FS. As shown in Figure 7(a) and (b), the degradation of dye was less than 20% in the presence of \( \text{H}_2\text{O}_2 \), around 15% in the presence of FA, negligible when exposed to sunlight, 22% in the presence of FA+ \( \text{H}_2\text{O}_2 \), 50% with sunlight + \( \text{H}_2\text{O}_2 \), very less in the presence of FA and sunlight, 87% in the presence of fly ash+ \( \text{H}_2\text{O}_2 \) and sunlight within 120 min.

2.2.2. Effect of variation of FA

The effect of FA dose on the degradation of the dye was observed in the range of 0.05–1 gm and shown in Figure 8(a). With the increase of FA dose, degradation and decolourization efficiency increased till certain limit (0.1 gm) after that it was decreased. The optimum amount of FA was 0.1 gm resulting in 92% degradation in 75 min and 97% decolourization in 15 min. At higher
FA concentration, a relative decrease in degradation and decolourization rates were observed may be due to the adsorption of both $\text{H}_2\text{O}_2$ and dye molecule on separate particles rather than at the adjacent sides of the same particle and thereby not reacting to each other (Feng et al. 2003; Catalkaya, Sengul 2005; Tony et al. 2008). This reduction can also be explained due to the fact that, at higher concentration of iron than the optimum, the hydroxyl radical initial formation rate was so high that most of them were consumed by the side reactions.

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**Fig. 8.** Percentage degradation and decolourization of RB5 at (a) varying concentration of FA (b) varying concentration of $\text{H}_2\text{O}_2$.

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**Fig. 9.** SEM micrograph and EDS pattern of a) used FA b) used FS, during photo-Fenton treatment of RB5.
before they could be utilized for the mineralization of the compound (Hsueh et al. 2005).

2.2.3. Effect of $\text{H}_2\text{O}_2$ concentration

In the presence of FA, the influence of $\text{H}_2\text{O}_2$ concentration on the heterogeneous photo-Fenton degradation of the dye was also investigated with different levels of $\text{H}_2\text{O}_2$ concentration (0.44, 0.88, 2.2, 6.61 and 8.82 mM) while keeping other operating parameters constant (FA = 0.1 gm, pH 3, $C_0 = 100$ mgL$^{-1}$). From the Figure 8 (b) it can be illustrated that the effective degradation (90%) was achieved within 30 min and decolourization (95%) within 10 min with optimum dose of 2.2 mM. Further increment in the dosage of $\text{H}_2\text{O}_2$ leads to decrease in the degradation rates. This reduction may be explained by the so-called hydroxyl radical scavenging effect.

The above study indicated the potential use of FS and FA as an alternative source of iron in photo-Fenton process for the treatment of RB5 dye. Effect of various reaction parameters on the degradation and decolourization efficiency was observed. The SEM-EDS for used FS and FA is shown in Figure 9(a) and (b) and data is shown in Table 3 and 4. The reduction in the composition of iron and aluminium confirmed their participation in the photo-Fenton reactions.

Table 3. Composition of FS after used in photo-Fenton process

<table>
<thead>
<tr>
<th>Element</th>
<th>C K</th>
<th>O K</th>
<th>Na K</th>
<th>Mg K</th>
<th>Al K</th>
<th>Si K</th>
<th>Ca K</th>
<th>Ti K</th>
<th>Fe K</th>
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<tr>
<td>Weight %</td>
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<td>50.50</td>
<td>1.42</td>
<td>1.06</td>
<td>5.49</td>
<td>23.37</td>
<td>0.64</td>
<td>0.51</td>
<td>6.15</td>
<td>100</td>
</tr>
<tr>
<td>Atomic %</td>
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<td>59.12</td>
<td>1.16</td>
<td>0.82</td>
<td>3.81</td>
<td>15.58</td>
<td>0.30</td>
<td>0.20</td>
<td>2.06</td>
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Table 4. Composition of fly ash after used in photo-Fenton process

<table>
<thead>
<tr>
<th>Element</th>
<th>C K</th>
<th>O K</th>
<th>Al K</th>
<th>Si K</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight %</td>
<td>8.33</td>
<td>61.12</td>
<td>1.54</td>
<td>29.02</td>
<td>100</td>
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<tr>
<td>Atomic %</td>
<td>12.38</td>
<td>68.17</td>
<td>1.02</td>
<td>18.44</td>
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</table>

Fig. 10. Percentage degradation and decolourization of RB5 at a) different FA to FS ratio b) different FS to FA ratio
2.3. Photo-Fenton studies using mixture of FS and FA as iron source

2.3.1. Effect of FS concentration keeping FA constant

To ascertain the effect of FS in oxidizing RB5, a series of experiments were conducted by varying FS concentration in the ratio of Ash: Sand = 1:1, 1:2, 1:4, 1:6, 1:8, 1:10 and 1:12. The influence of FS dosage on degradation and decolourization efficiency is illustrated in Figure 10(a). The degradation and decolourization rate of RB5 decreased with increasing amounts of FS. More than 95% degradation and decolourization rates were achieved with the ratio Ash: Sand = 1:2, where amount of Ash and FS were 0.05 gm and 0.1 gm respectively.

2.3.2. Effect of FA concentration keeping FS constant

On similar trend, the effect of varying FA keeping FS and other parameters constant on the degradation and decolourization of RB5 was investigated in the ratio of Sand: Ash = 1:1, 5:1, 5:2, 5:3, 5:4 and 10:1 and the results were presented in Figure 10(b). The results indicated that the extent of degradation and decolourisation was significantly influenced by the dosage of FA. Decrease in the degradation and decolourization efficiency was observed with increasing amount of fly ash. The optimal ratio value for the degradation (92%) in 60 min and decolourization (90%) in 30 min for the dye was achieved at Sand: Ash = 10:1 where FS and FA were taken 0.5 g and 0.05 g respectively.

The above study concluded that the combination of FS and FA gave better results in the terms of degradation and decolourisation along with the reduction in the treatment time. For combination of FS and FA, degradation (90%) after 25 min and decolourisation (97%) within 10 min was achieved whereas, for the same degradation (90%) and decolourisation (90%) FS alone took 70 min and 45 min respectively and FA took 30 min for 90% degradation and 15 min in 93% decolourisation.

Thus, combination gave the better prospects for the use of waste materials like FS and FA to be used as potential iron source in the photo-Fenton process as pre or post treatment options for the degradation of priority pollutants like dyes.

Conclusions

In this study, attempt has been made for using FS, FA and their combination as heterogeneous catalyst in the photo-Fenton process for the degradation of RB5.

While using FS as heterogeneous catalyst the maximum degradation and decolourization 95% and 97% respectively was achieved and 99% degradation and decolourization was achieved using FA, thus proposing value addition to waste.

When combination of FS and FA was tried, 99% degradation and decolourization of RB5 was achieved with different ratios of FA and FS. Thus, presents viable options for using waste materials as source for environmental remediation.

The advantages are high degradation rates (99%), simple handling, environmental friendly, and low cost (waste as an iron source), which otherwise consumes expenses towards its disposal/land filling.

References


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