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RESEARCH ARTICLE

Iron(III)-mediated photodegradation of orange green dye

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Abstract

The degradation of Orange Green (OG) by excitation of iron(III) in aqueous medium was investigated under UV, visible and solar irradiation. The degradation efficiency was influenced by the pH of the solution, initial concentration of OG and initial concentration of Fe(III). The progress of removal of OG from solution was monitored by recording the change of absorbance at λ_{max} = 478 nm with time. The initial concentration of OG was varied from $1.00\text{x}10^{-4}$ molL^{-1} to $2.50\text{x}10^{-4}$ molL^{-1}and pH was varied from 1.0 to 2.2. The range of initial concentration of Fe(III) was from $2.00\text{x}10^{-4}$ molL^{-1} to 2.00 x10^{-2} molL^{-1}. As the concentration of Fe(III) was increased, percent degradation increased rapidly until the concentration of Fe(III) reached a value of 0.005M. Beyond this concentration, percent degradation becomes steady and independent of concentration of Fe(III). Percentage of degradation was increased with increasing pH and was found to be maximum when pH was 2.2 but percent degradation decreased with increasing concentration of dye. The percent degradation was found to be higher when irradiated under solar light than under the UV and visible light.

Introduction

In Bangladesh there are many textile and dyeing industries at Narsingdi, Gazipur, Narayanganj and Manikganj. One of the major problems in the country is the release of industrial effluents from the textile industries which contain different types of dyes. This release in the aqueous medium is a major threat to the ecosystem [1]. It causes a severe damage to the aquatic lives due to the toxic, nonbiodegradable and carcinogenic nature of these dyes. Azo dyes, which are the largest class among these pollutants [2, 3], are mostly constituted by aromatic rings linked together by –N=N– bonding.

Various physical [4-7], chemical [8-10] and biological [11, 12] methods are used to remove dyes from wastewater. One of the most important emerging technologies is the advanced oxidation process which is described as the oxidation process based on the generation of hydroxyl radical intermediates. The direct photolysis of H_2O_2 by the photon of wave length shorter than 370nm produces two hydroxyl radicals that can oxidize most organic pollutants. AOPs based upon hydrogen peroxide, ozone and ultraviolet radiation have been well investigated [13,14]. Fenton's reagent (hydrogen peroxide activated with Fe(II) salts) is very suitable for the oxidation of toxicants present in wastewater.

Recently, the importance of system with Fe(III)-aqua complexes for the photogeneration of hydroxyl radicals [15,16] has been pointed out. Unlike the photo-Fenton system in the Fe(III) aqua complexes no addition of hydrogen peroxide is needed. Faust et al. [17] and Benkelberg et al. [18] found that Fe(III)-aqua complexes absorb a fraction of the available solar light up to 500nm. Therefore, Fe(III)-mediated photogeneration of hydroxyl radicals is expected to be an efficient and inexpensive method for wastewater treatment. It is known that ferric ion in aqueous solution has the tendency to form aqua complexes. It has been established [19, 20] that, the hydrolysis is governed in its initial stages by the following equilibrium constants:

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+ \qquad K_1 = 1.39\text{x}10^{-3}\text{molL}^{-1}$$

$[Fe(H_2O)_5(OH)]^{2+} \rightleftharpoons [Fe(H_2O)_4(OH)_2]^{+} + H^{+}$ $K_2 = 3.12 \times 10^{-4} molL^{-1}$

Due to above equilibria the concentration of H^+ increases suggesting that the extent of hydration will be large when the concentration of H^+ will decreases meaning that the extent of hydration will be large at high pH (higher than 1)
Of the two mentioned complexes the dominant species could be $[Fe(H_2O)_5(OH)]^{2+}$ because of larger value of equilibrium constant. The following equation shows the production of hydroxyl radicals [21]:

$$[Fe(H_2O)_5(OH)]^{2+} + h\nu \rightleftharpoons [Fe(H_2O)_6]^{2+} + OH^{\cdot} \qquad (1)$$

Hydroxyl radicals can cause mineralization of the pollutants completely. It has been reported that hydroxyl radicals generated upon excitation of Fe(III) aqua-complexes of low concentrations were useful for the degradation and mineralization of the organic pollutants [15,16,22-27]. The advantages of the photodegradation process as an oxidative treatment are economic, rapid and simple to handle.
The objectives of present study is to investigate how and to what extent the photogenerated hydroxyl radicals from Fe(III)-aqua complexes degrade a typical textile dye orange G under different experimental conditions.

Material and methods

Materials

Orange G(Commercial grade) obtained from BDH, England. All other chemicals were purchased from Merck, Germany. The distilled water was used throughout the present study**.**

Methods

Stock solution

1×10^{-3} $molL^{-1}$ Orange G solution was prepared in 100.0mL volumetric flask with distilled water. Required dilute solutions were prepared from this stock solution. The concentration range of Orange G used for experiment was from 4×10^{-5} $molL^{-1}$ to 2.5×10^{-4} $molL^{-1}$.
0.1 $molL^{-1}$ $Fe(NO_3)_3$ solution was prepared in a 100.0mL volumetric flask. Further dilution was made whenever necessary. The concentration range of Fe(III) solution used for the experiment was from 2×10^{-4} $molL^{-1}$ to 2×10^{-2} $molL^{-1}$.

Photodegradation

All the experiments were carried out in a beaker used as the reactor. The source of radiation was comprised of a lamp emitting UV radiation of 254 nm, visible light and solar light. The reactor was placed on a magnetically stirred plate and the distance of the solution surface from the lower part of the lamp was 15.5cm. The total system was enclosed in a wooden box called lamp house. Inside surfaces of the lamp house was covered by Aluminum foil to avoid the absorption of light (exception was for solar light). For solar light, the reactor was also placed on a magnetically stirred plate under natural environment. The time for the experiments was chosen between 12.00 am to 2.00 pm of sunny days in the month of june-2012.
In case of photodegradation of OG, 50.0mL reaction mixture containing OG and $Fe(NO_3)_3$ was irradiated by different light sources in the lamp house described before. Certain portion of reaction mixture was collected at different time intervals during irradiation. It was then centrifuged (Laboratory centrifuge machine-3000 cps, Heka, BHG) and analyzed using UV-visible spectrophotometer to determine the concentration of OG.

Results and Discussions

Effect of Fe(III) concentration

To investigate the effect of the concentration of Fe(III), experiments were carried out with varying concentration of Fe(III) under visible light irradiation which is shown in Fig 1. With increasing the concentration of Fe(III) ions, the percent degradation of OG increases. During these experiments the OG concentration was fixed at 2×10^{-4} M. It is likely that higher is the concentration of Fe(III) ions, more is the production of $^{\cdot}OH$ radical. It is the hydroxyl radical which initiate the degradation process. So percentage of degradation increases with increasing concentration of Fe(III) ions. The Fig 2 shows the sharp increase in percent degradation within a short time when the concentration of Fe(III) was increased from 0 to 0.001M. This might be due to the rapid formation of $OH^{\cdot}$ radical via reaction (1). The percent degradation reached steady value after 0.005M concentration (Fig 2) and remained unaffected by further increase of Fe(III) ion. This is probably due to the steady concentration of $^{\cdot}OH$ radicals obtained at higher concentration (concentration >0.005M) of Fe(III). This can be explained by the following mechanism:

$$Fe(OH)^{2+} + h\nu \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe^{2+} + OH^{\cdot}$$

$$\mathrm{OH\cdot + OG} \xrightarrow{k_2} \mathrm{Product}$$

Where $\mathrm{Fe(OH)^{2+}}$ refers to $\mathrm{[Fe(OH)(H_2O)_5]^{2+}}$.
Applying steady state approximation to the concentration of hydroxyl radicals,

$$\frac{d[\mathrm{OH.}]}{dt} = \mathrm{k_1[Fe(OH)^{2+}]I - k_{-1}[Fe^{2+}][OH^{\cdot}] - k_2[OH^{\cdot}][OG] = 0}$$

$$\mathrm{[OH^{\cdot}]} = \frac{\mathrm{k_1[Fe(OH)^{2+}]I}}{\mathrm{k_{-1}[Fe^{2+}] + k_2[OG]}} \qquad \text{(I)}$$

Where, I= intensity of incident light
When $\mathrm{k_{-1}[Fe^{2+}] \gg k_2[OG]}$ (100 times greater) then,

$$\mathrm{[OH^{\cdot}]} = \frac{\mathrm{k_1[Fe(OH)^{2+}]I}}{\mathrm{k_{-1}[Fe^{2+}]}} \qquad \text{(II)}$$

At higher concentration of $\mathrm{Fe(OH)^{2+}}$, the reverse reaction (1) becomes significant and the ratio $\frac{\mathrm{k_1[Fe(OH)^{2+}]I}}{\mathrm{k_{-1}[Fe^{2+}]}}$ becomes constant. So the concentration of hydroxyl radical reaches to a steady value.

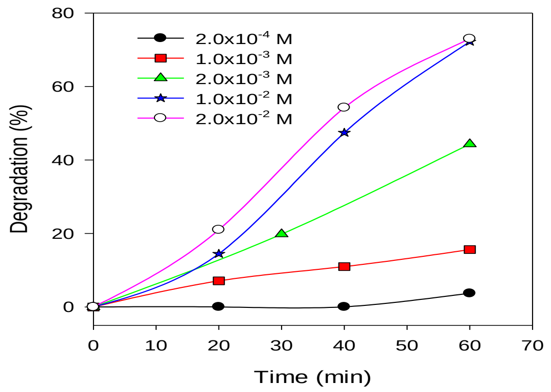

Fig 1: A plot of percent degradation of OG as a function of time at various concentrations of Fe(III) under visible light.

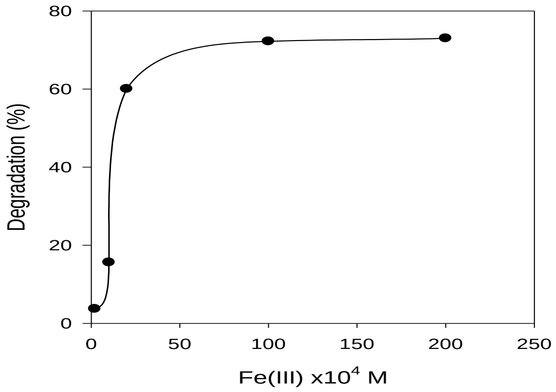

Fig 2: A plot of percent degradation of OG as a function of concentration of Fe(III) for 60 minutes irradiation.

Effect of OG concentration

After optimising the concentration of Fe(III) which was fixed at 2.0×10^{-2} M, the photodegradation of OG was carried by varying the concentration of OG under visible light irradiation. The results in Fig 3 show that the percent degradation of OG decreases with increasing concentration of OG. Since a fixed amount of Fe(III) catalyst produces fixed amount of $^{\cdot}$OH radicals and these radicals can only attack a proportional amount of OG. As the concentration of OG increases the number of available sites in OG to be attacked by the radical also increases. But the fixed amount of catalytic reagent $^{\cdot}$OH cannot degrade the extra OG and as a result percentage degradation falls as shown in Fig 4. This can also be explained by equation (I). These results are in agreement with BANSAL et al [28], who studied the UV-assisted degradation of OG in presence of $\mathrm{H_2O_2}$.

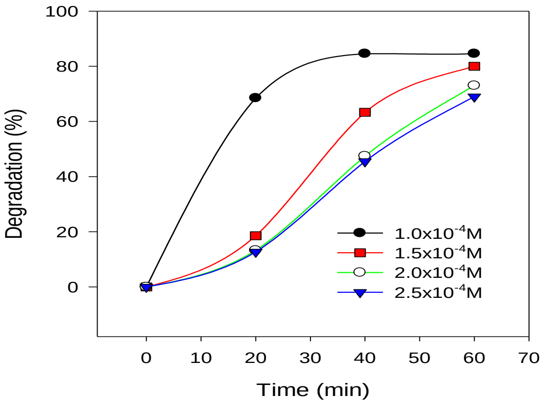

Fig 3: A plot of percent degradation of OG as a function of time at various concentrations of OG.

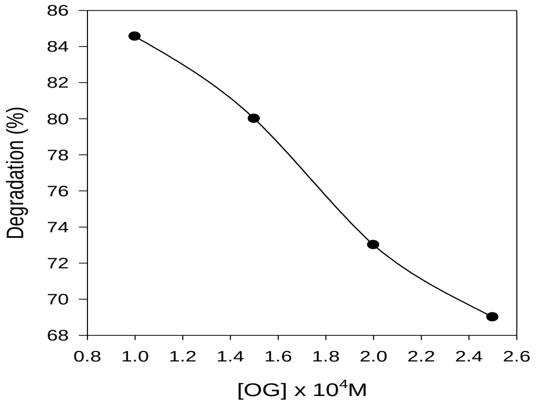

Fig 4: A plot of percent degradation of OG as a function of concentration of OG for 60 minutes irradiation.

Effect of pH

Effect of pH on the degradation of OG by the use of Fe(III)-aqua complex as a photocatalyst was investigated over the pH range of 1.0–2.2 under visible light irradiation. Fig 5 shows that photodegradation increases with increasing pH of the solution within the range. This increase may be due to more availability of $^{\cdot}OH$ radical formed from the complex $Fe(OH)^{2+}$ suggesting that the complex formation is favored by this pH range. At pH higher than 2.2, precipitation of $Fe(OH)_3$ was observed [15-18]. So photodegradation was not carried out. At low pH (pH<2.2) the concentration of $[Fe(H_2O)_5(OH)]^{2+}$ is low because of the presence of excess H^+ ions. Hossain et al [29] was also studied the photodegradation of OG by Fe(III)-aqua complex and found similar results.

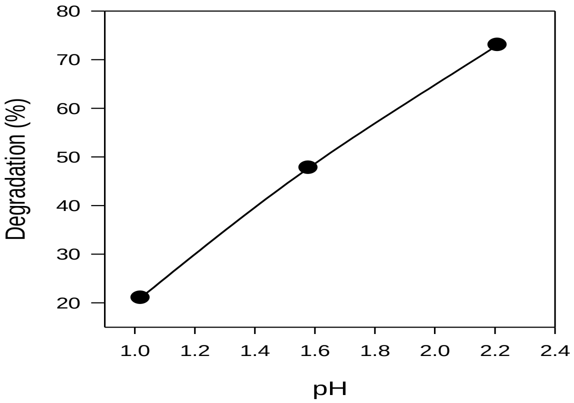

Fig 5: Effect of pH on the degradation of OG with $Fe(NO_3)_3$ after 60 minutes irradiation.

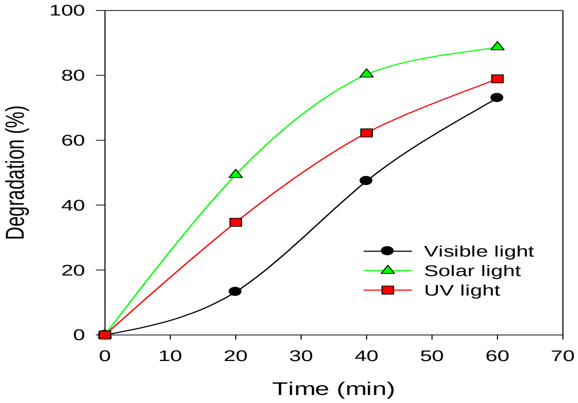

Fig 6: Percent degradation of OG with $Fe(NO_3)_3$ in presence of different light sources.

Effect of light sources

To investigate the effect of different light sources, experiments were carried out using UV, visible and sun light which is shown in Fig 6. In this case optimum concentrations of OG and $Fe(NO_3)_3$ were 2×10^{-4}M and 2×10^{-2}M respectively. Highest percentage of degradation of OG was found by irradiating the dye in sun light and visible light shows lowest percentage of degradation. This may be due to the fact that $Fe(H_2O)_5(OH^{)}]^{2+}$ can absorb light up to 500 nm[17,18] which is available in sunlight. These results are in agreement with the results of BANSAL et al [28] who found that the degradation of OG was increased with increasing light intensity.

Conclusion

Degradation of Orange Green (OG) has been carried out by Fe(III)-aqua complex under UV, visible and solar irradiation. Photodegradation of OG by Fe(III)-aqua complex was found to be affected by pH, concentration of Fe(III) and OG and by different light sources. The pH was varied from 1.02 to 2.2. Because of precipitation of $Fe(OH)_3$ at high pH (higher than 2.2) the experiments were not carried out beyond the pH of 2.2. With increasing the concentration of Fe(III) the percent degradation increased and reached a steady value after concentration of

$0.005 molL^{-1}$ but percent degradation decreased with increasing concentration of OG. Fe(III) aqua complex is an effective photocatalyst under solar irradiation. The above results suggests that Fe(III) mediated photodegradationcan be effectively used for the destruction of textile dyes present in the industrial effluents.

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