DEGRADATION OF MONO-AZO DYE IN AQUEOUS SOLUTION USING CAST IRON FILINGS

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Abstract

The mono-azo dye, Orange II, solution was substantially degraded with cast iron particles under varied conditions of experimental variables such as pH, initial dye concentration and cast iron dosage.At all solution pH studied, the degradation efficiency achieved was > 90%. With an initial dye concentration of 100 mg/L and optimum cast iron load of 28.56 g/L, the optimum degradation efficiency of 97.63% was achieved at pH 3. With same cast iron load and solution pH, more than 95% dye degradation efficiency was achieved at different initial Orange II concentrations ranging from 50-500 mg/L. The efficiency of cast iron particles in degrading Orange II dye was compared with that of pure elemental iron used in other study. Cast iron particles showed better degradation efficiencies than elemental iron that too at relatively lower dosages. Ultimately, from the results it can be inferred that cast iron fillings can be successfully applied to treat textile effluents containing high dye concentration and treatment efficiency can be enhanced by optimizing the reaction conditions.

Index Terms: *azo dyes, Orange II, degradation efficiency, cast iron fillings*

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1. INTRODUCTION

Textile dyeing industries have long been one of the most important industries in the world. According to an estimate, around 0.7 million tons of dye are used every year of which 50% are azo dyes [1]. Of the total dye produced, 15% is lost during the dyeing process [2]. Dyes being tinctorially stronger are visible in water at concentrations as low as 1 ppm [3]. Available literatures points that dye containing effluent are more mutagenic and toxic when compared to other industrial discharges [4]. Researchers have shown that azo dyes released into ground and surface waters from textile discharges contribute to mutagenic activity [5,6]. Besides, the release of coloured wastewater in the ecosystem is a remarkable source of aesthetic pollution, eutrophication, and perturbations in aquatic life [2].Several chemicals found in dye-bath effluent are toxic, carcinogenic, mutagenic, or teratogenic to various life forms. The human health impact of dyes, especially azo dyes and their degradation products have caused concern for a number of years, with legislation controlling their use, being developed in a variety of countries [7]. Increasingly, the environment and subsequent health effects of azo dyes released in textile industry wastewater are becoming subject to scientific scrutiny. It is hence not surprising that removal of these compounds has now-a-days become a major environmental concern.

Many physical and chemical treatment processes have been developed in scientific laboratory but their practical applicability is restricted either by cost or efficiency and cannot be adopted as an exclusive method.Conventional biological treatment methods alone generally are ineffective insofar as complete azo dye degradation is concerned[8]. Since biological treatment methods are still the cheapest option available, efforts should be made to develop an effective pretreatment technology that could transform the azo dyes into easily bio-decomposable compounds.

Reductive transformation of pollutants using cast iron filings is widely gaining attention for environmental remediation. Cast iron filings are cheap and easily available strong reducing agent. The literature substantially reports the applicability of cast iron filings in treating wastewater contaminated with chlorinated compounds [9], nitroaromatic compounds [10], heavy metals [11], explosives[12] and dyes[13], etc. Among these pollutants azo dyes are considered as most susceptible to metallic reduction [14], thus, if the treatment conditions are optimized cast iron filings can serve as an effective pretreatment alternative. In this study, treatment of synthetic wastewater containing mono-azo dye Orange II has been carried out using cast iron filings. This study intends to optimize the key reaction parameters that could affect the applicability of cast iron filings for treating azo dye-containing wastewater in large scale.

2. MATERIALS AND METHODS

2.1. Dye

Commercially available mono-azo dye Orange II (M.W.-350.32)which is a widely used anionic monoazo-dye [15] was chosen as a model of the hydro soluble phenylazonaphthol dyes due to its resistance to biological degradation.AO7 was purchased from Atul Ltd. (India) and was used as received. The dye solutions in a 1cm quartz cuvette were scanned over the wavelength range 200–800nm using a UV–visible spectrophotometer (UV-1800 series, Shimadzu, Japan) for determination of the wavelength of maximum absorbance (λ max).

2.2 Preparation of Cast Iron Fillings

Commercially available cast iron rod was chipped on a lathe machine and then ground into iron filings in a dough-size ball mill. The filings were sieved and those between 40 (425 μm) and 80 (212 μm) mesh sizes were retained for use. Cast iron fillings, thus produced, was washed 5-6 times with N2-sparged 1N HCl with periodic shaking. Then it was rinsed 10-12 times with N2-sparged deionised (Milli Q) water. The washed fillings were rinsed twice with acetone to remove moisture. Again it was rinsed twice with 95% pure ethanol and dried for 1 hour. This treatment yielded black metallic filings with no visible rust on the surface. Fillings were stored in a vacuum desiccator until use in various experiments.Surface area of the treated filings was determined by BET (N2) analysis using a BET surface area analyzer (NOVA 4000e, Quanta chrome Instruments, USA) to be 1.4 m2/ g.

2.3 Experimental Procedure

Time series batch experiments were carried out in 35 ml capacity glass vials with screw caps (Borosil, India). All dye solutions were prepared using deionized (Milli Q) water and all reagents utilized were of analytical purity. The solution pH was adjusted to the desired levels using HCl (0.5M) or NaOH (0.1 M) with a pH meter (Digital pH meter 111, EI, India). For proper mixing, the vials were placed on a test tube rotator (Rotospin, Tarsons, India), at 30 rpm, keeping the axis of vials horizontal. Temperature was 25 ± 2○C for all experiments.
Vials were removed from the rotator in duplicate (along with a control) at specified times for sampling and analysis and were put on a magnet to allow iron particles to settle down quickly. Supernatant samples were taken out from vials and filtered through GF/C filter paper (1.2 μm nominal pore size, What man, Springfield Mill, England).

2.4 Analytical Procedure

Efficiency of cast iron fillings for the degradation of Orange II was assessed in terms of decolorization efficiency (%) as follows:

$$\text{Degradation efficiency (\%)} = [1 - A_t/A_0]\times 100\% \qquad (1)$$

Where At = absorbance of solution at time‘t’ of treatment,

A0 = absorbance of untreated solution.

3.0 RESULTS & DISCUSSION

3.1 UV-Vis Scan

The UV-vis spectra of Orange II scanned over wavelength range of 200 to 800 nm is shown in Fig.1. Different absorbance peaks exhibit different structural units and groups of the dye molecule.Orange II is characterized by one main band in visible region, with its maximum absorption at 484 nm, and two bands in ultraviolet region located at 229 nm and 310.5 nm. These observed peaks correspond to chromophore containing azo linkage, benzene ring and naphthalene ring, respectively [16].

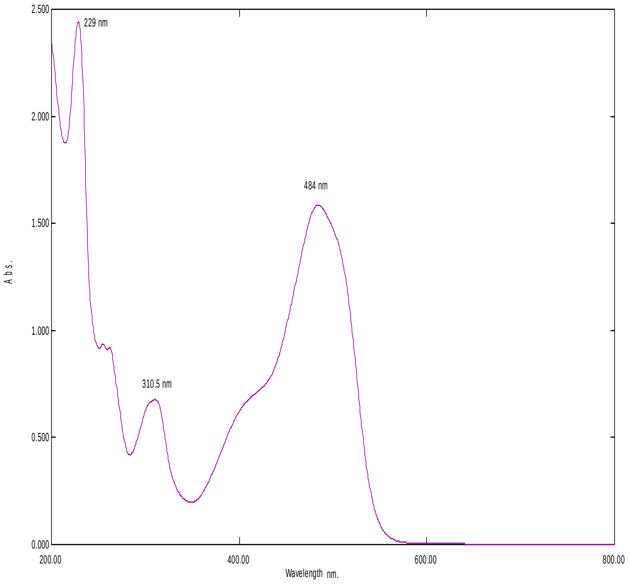

Fig.1: UV-Vis spectra of Orange II azo dye

3.2 Effect of Solution pH

Solution pH has been considered as one of the important factors in governing the reduction of contaminants by elemental iron, therefore the effect of initial solution pH on the decolorization of Orange II was studied, and the results are shown in Fig.2. The degradation efficiency crossed more than 90% within 5 min of treatment.Final Orange II degradation efficiency after 60 min of treatment was 97.63%,97.11%, 96.97%, 95.14%, 93.95%,for pH 3, pH 4, pH 5, pH 6 and pH 7, respectively. As the solution pH increased decolorization efficiency decreased.When dye molecule collides with elemental iron, elemental iron, as an electron donor, loses electrons, the dye molecule, as an electron acceptor, accepts electrons, and combines with H+to form a transitional product. This product receives electrons from elemental iron and combines with H+ again, finally turning into terminal products. With more H+ in acid solution than that in alkaline solution, the reaction in acid solution is easier [17].

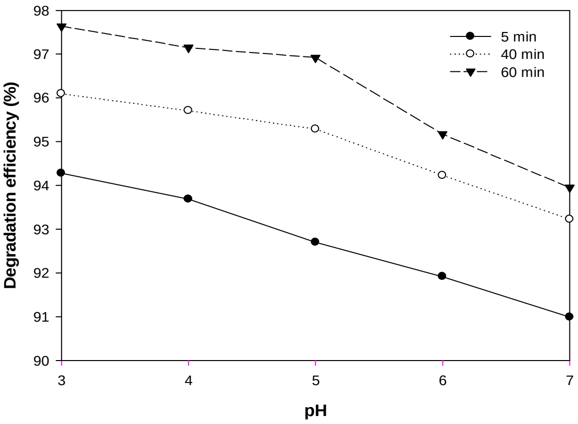

Fig.2: Effect of different pH values on degradation of Orange II dye solution (Initial conditions:cast iron dose= 28.56g/Ll;Orange II conc.=100 mg/L; mixing speed-30 rpm)

3.3 Effect of Initial Dye Concentration

The effect of initial concentrations of Orange II on its degradation efficiency were evaluated at a concentration range of 50 mg/L to 500 mg/L using 28.56 mg/L cast iron dosage at pH 3. As shown in Fig. 3, the degradation efficiencies achieved after 5 min was decreasing with increasing initial Orange II concentration, i.e., 97.21, 94.81, 92.48,75.18, 57.07 and 47.63% for initial dye concentrations of 50 mg/L, 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L and 500 mg/L, respectively. This suggests that the decolorization is adsorption controlled process [18]. The final efficiencies were greater than 95% after 60 min of treatment for all concentrations of Orange II studied.

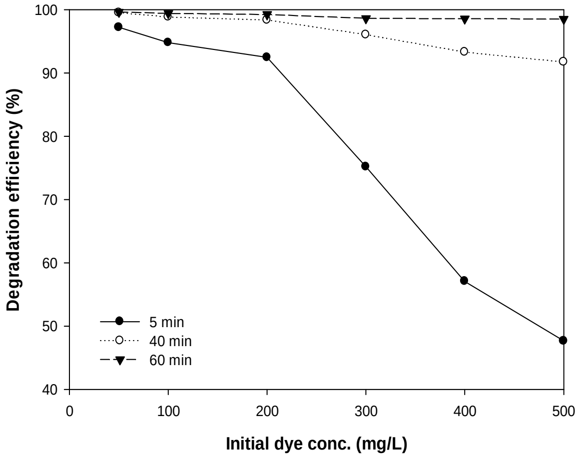

Fig. 3: Effect of different initial dye concentration on degradation of Orange II dye solution (Initial conditions: cast iron dose= 28.56g/L; pH- 3.00; mixing speed-30 rpm)

3.4 Effect of Cast Iron Load

The effect of the cast iron dosage on on Orange II removal efficiency,shown in Fig. 4, indicates that Orange II degradation efficiency increased with the increase of the cast iron load. From the experimental data 54.93%, 75.13%, 96.25%, 96.79% and 96.91% degradation efficiencies within first 5 min, and96.36, 97.63, 99.42, 99.21 and 99.21%after 60 min by cast iron doses of 7.14g/l, 14.28g/l, 28.56g/l, 42.84g/l and 57.12g/l, respectively. Increasing the load of cast iron provided substantially more active surface sites to accelerate the initial reaction, resulting in more iron surface collision with more azo dye molecules to enhance Orange II degradation. However, highest degradation efficiency was achieved at cast iron dosage of 28.56 g/L. This unusual precept can be attributed to the fact that the presence of excessive iron in the acidic solution system could be detrimental since the final pH of the system could reach higher values thereby decreasing the degradation rate [19].

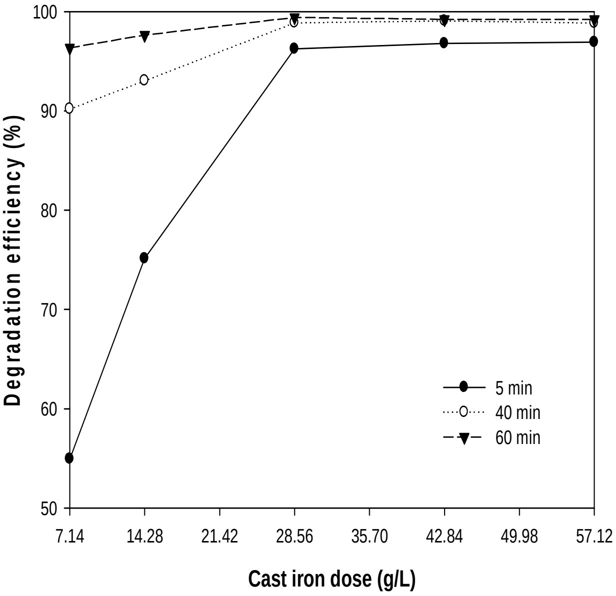

Fig. 4: Effect of different cast iron dosage on degradation of Orange II dye solution (Initial conditions: solution pH -3; Orange II conc.= 100 mg/L; mixing speed-30 rpm)

3.5 Comparison of Efficiencies of Cast Iron Fillings and Pure Iron

Table 1 shows the comparative degradation efficiencies of Orange II using pure elemental iron as reported by Mu et al.[18], and cast iron fillings reported in this work. Mu et al.[18] have reported highest degradation efficiency of 90-95% for 101.5 mg/L Orange II adding 66.6g/L of pure iron after 80 min of reaction time. Whereas in this study greater than 99%

degradation efficiency could be achieved for 100mg/L Orange II using fairly low cast iron loading of 28.56 g/L within 60 min of reaction time. Also, the mixing speed was kept 4 times lower at 30 rpm in this study compared to 120 rpm reported by Mu et al.[18]. In addition, cast iron fillings showed significantly higher degradation efficiencies at all pH ranges studied. This greater ability of cast iron to degrade Orange II could be attributed to the presence of graphite inclusions embedded in the iron matrix which serves as anon-reactive adsorption site[9,20,21]. Thus, adsorption and reduction takes place simultaneously on cast iron surface.

Table 1: Comparison of degradation efficiency of cast iron and zero valent iron studies

Author	Iron type	Dosage (g/L)	Dye	Mixing rate (rpm)	Temp (°C)	Reaction time (min)	Conc. (mg/L)	pH	Efficiency (%)
Mu et al.[18]	Micro-ZVI	66.6	Orange II	120	30	80	49 101.5 199.5 101.5 101.5 101.5 101.5	4 4 4 3 5 6 7	< 90 ~75 75 90-95 70 60-70 60
This work	Micron sized Cast Iron	28.56	Orange II	30	25±2	60	50 100 200 100 100 100 100	3 3 3 4 5 6 7	>99 >99 >99 97 ~97 95 ~94

CONCLUSIONS

In this work, the parameters affecting the reductive degradation of Orange II dye were investigated. Although cast iron particles were found to be capable of degrading more than 90 % of Orange II at all pH examined within 5 min of treatment time, optimum degradation efficiency of 97.63% was achieved at pH 3 after 60 min. More than 50% dye degradation was achieved at all cast iron dosages within 5 min and the efficiencies exceeded 90% at all dosages after 40 min. At all the initial Orange II dye concentration studied, more than 95% degradation efficiencies could be achieved using cast iron dosage of 28.56 g/L. This indicates that cast iron can be effective even at the wide range of dye concentration in textile effluent. Comparative assessment of degradation efficiencies of cast iron and pure elemental iron reveals greater capability of cast iron to treat dye containing wastewater.Apart from the experimental results, the fact that cast iron is available at a fraction of the cost of the high purity iron makes it a more ideal cost effective alternative for practical treatment applications.

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