

Research Article

Novel Photo-Fenton Oxidation with Sand and Carbon Filtration of High Concentration Reactive Dyes both with and without Biodegradation

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Abstract

There is an increasing need to provide rural textile dye operations in developing nations with an effective and low-cost method to clean dye wastewater. Such operations often have no choice in the location of their wastewater disposal due to their lack of funds and influence in the industry, resulting in wastewater disposal that is detrimental to environmental safety. Photo-Fenton oxidation, an advanced oxidation process used to degrade low-concentration textile dye wastewater, has shown promise using expensive chemicals in laboratory-scale projects. Aerobic biodegradation, a common biological treatment method used in large-scale low-concentration textile industrial applications, generates large amounts of hazardous biological waste. This paper presents successful decolorization of high-concentration reactive dye wastewater using a wide range of temperatures and solar irradiances in two locations for the first time. To fully degrade dye wastewater, full oxidation times combined with sand and carbon filtration rank more important than different iron surface areas. UV-visible spectrometry, GC/MS, and ICP techniques along with measured COD levels were used to support these findings. This study is expected to provide a low-cost method to clean high concentration and sand and carbon filtration in a reactor and the filter that is constructed of recycled rusty metal and locally available sand.

Keywords: Reactive dye; Photo-fenton oxidation; Biodegradation; Filtration; Scrap iron

Introduction

Clothing is an essential part of daily human life worldwide, but rarely any thought is given to how clothing is actually made. Before fabric is sewn into clothing, it must be dyed. Much of the cloth manufacturing process is often outsourced to developing countries, where it is frequently located in rural communities. Rural dyeing communities exist in many countries throughout the world, including India, Morocco, Mexico, and Turkey. In these areas, the heavy pollution caused from the industry is not readily seen, but still is damaging to the environment. For example, India is the second-largest global producer of silk, employing over one million families, where the majority of silk dyeing is accomplished in small villages, in which a typical community contains small-scale silk dyeing businesses owned and operated by local families [1]. In central Bangalore, there are approximately 150 silk dyers that are currently using no wastewater treatment as well as many other small communities of cottage-scale silk dyers surrounding the city. Most of the operation of dyeing silk saris there occurs in small communities that are then saddled with environmental problems due to the high levels of chemicals in the dyes. The fundamental problem is that once the fabrics are dyed, the dye waste is discharged back into the community's water source or thrown directly onto the ground, where it can seep into the groundwater that feeds the local water systems. Many of the residents in these communities are very poor and are forced to use the contaminated water for their daily needs.

Reactive dyes have a very high stability that sustains their color once the textile is washed. As a result, they are used frequently in the silk dyeing industry and account for 32% of all dye operations. In these operations, only 70% of the dye is absorbed during a dye job, leaving 30% to enter the waste stream [2]. Considering that the homespun silk industry in places such as rural Bangalore currently use no treatment for their dye wastewater prior to discharging it into streams or onto land, the typical textile wastewater entering the groundwater of the area contains a pH ranging between 7-9, Biological Oxygen Demand (BOD) 80-6000 mg/l, Chemical Oxygen Demand (COD) 150-12000 mg/l, Total Suspended Solids (TSS) 15-8000 mg/l, Total Dissolved Solids (TDS) 2900-3100 mg/l, chloride levels between 1000-1600 mg/l, total Kjeldahl Nitrogen from 70-80 mg/l, and color from 50-2500 color units [3].

Dye effluent has very complex molecular composition that when discharged to the natural environment can cause irreparable harm to ecosystems. The total discharge of dye effluent is more than 0.01 metric tonnes per annum because of the high production rate of the industry. This pollution, if left untreated, thereby creates a huge impact on flora and fauna. Reactive red dyes are types of azo dyes that continue to be used in some countries in great quantities although they have been banned in many developed countries of the world. These dyes have one or more double nitrogen bonds in their chemical structure bonded to aromatic rings; this is one of the most difficult synthetic linkages

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to break [4,5]. It is also reported by these researchers that Fenton's reagent, discovered a century ago, shows great promise in breaking these environmentally-destructive bonds through using hydroxyl radicals. However, the use of iron as a catalyst in the reaction tends to create additional unforeseeable pollutants in solution. It is also reported that removal of azo dyes from solution is difficult, but the reaction that forms hydroxyl radicals removes 85% of COD and complete color removal in 20-40 minutes [6].

Residents of rural areas would certainly benefit from reductions in the contamination by the dye effluents generated in their localities. For example, families in rural Bangalore expressed great interest in finding a system that would allow them to economically treat the dye wastewater [Personal Communications]. It is logical to conclude that there is need to develop a suitable methodology to meet the aspirations of these rural families throughout the world. Accordingly, to help achieve this goal, the authors took up this task in several stages (objectives), first with the proposal to test two methods to clean contaminated dye wastewater using very affordable materials that can be easily found in and around the homes of the dyers.

Large and medium dyers who produce 40,000-3,000,000 liters per day of dye effluent can afford treatment to include settling tanks, biodegradation, drying beds, sand and carbon filtration, reverse osmosis systems, etc. that costs between 0.003-0.005 USD per liter [Personal Communications], not including exorbitant infrastructure and equipment costs (including reverse osmosis) that exceed 30,000 USD. Small cottage-scale industries do not have the luxury or community support to get such a discount on their treatment. The aim of this study however, is still to create a low-cost treatment option that includes reasonably priced infrastructure. Table 1 displays a comparison of infrastructure and treatment costs of large and medium dyers compared with the sustainable photo-Fenton oxidation and filtration method for small-scale dyers. Preliminary work has been done to develop a system for a small-scale dyer. The costs determined in that project are reflected there.

In the present study, results of the treatment of Reactive Red 120, Reactive Yellow 81 and Reactive Blue 4 in laboratory scale experiments are presented. The two forms of treatment used were sustainable photo-Fenton oxidation with sand and carbon filtration and sustainable photo-Fenton oxidation with sand and carbon filtration coupled with biodegradation. Both of these techniques have been shown to be affordable, efficient methods of decolorizing dye wastewater using acid, hydrogen peroxide, iron scrap, and sunlight [7-11]. This work is the first of its kind to use (i) a 5 g/l dye concentration equivalent to effluent from cottage-scale textile dye industries, and (ii) sand filtration to raise the pH back to neutral and to separate the sludge formed during the oxidation process from the aqueous solution. To meet the objective to help poor communities in developing countries through the development of an economically viable and easily adoptable process, a system was designed and constructed from readily available, inexpensive (or scrap) materials. Accordingly, the laboratory study used sheet metal as its iron source, to create a rusty sheet metal container for a future demonstration project in rural places of not only India, but in other countries of the world.

With the success of this new technology and proper education, rural populations will be able to clean their dye effluent before discarding it to the environment, thereby reducing soil and ground water pollution. Alternatively, water could be reused in future dye batches thus decreasing their overall water consumption. It is expected that this laboratory-scale project will be successfully extended to a demonstration-scale project.

Experimental Methodology

The laboratory-scale treatment process encompassing eight stages was carried out both in India (National Environmental Engineering Research Institute (NEERI), Nagpur - hereafter referred to as 'India') and in the USA (University of Wisconsin-Milwaukee (UWM), Milwaukee, WI, USA). The Reactive Dye wastewater is (i) created in a 1-liter pot, (ii) acidified to pH 2.5-3.0 with hydrochloric acid, (iii) stirred and infused with pharmacy-grade 6% hydrogen peroxide (quantity listed in Tables 2 and 3), (iv) poured into the mobile photo-Fenton oxidation reactor that contains multiple pieces of rusty metal on its base, (v) left open to the sun for partial/full oxidation time (time listed in Table 4), (vi) poured through a sand filter to separate the iron/dye sludge from solution, (vii) filtered through activated carbon to absorb any remaining organics, and (viii) tested for color change, temperature, acidity (pH), concentrations of COD, any other organic material present, metals and ions, and biodegradability. It should also be noted that six main variables were used throughout the study to test their effect on treated water quality: (a) decolorization of different colors of dye (red, yellow, and blue) at a concentration of 5 g/L, (b) angle of incoming natural UV sunlight (India or USA), (c) volume of hydrogen peroxide (optimized according to color), (d) quantity of rusty iron (high iron of 645 cm², medium iron of 323 cm², low iron of 161 cm²), (e) time of oxidation (partial or full), and (vi) filtration (none, sand, sand and carbon).

Materials employed

Dyes: Following literature indicating that reactive dyes have been the leading silk dyes used by industry [2], this study considered three such dyes, Red 120, Yellow 81 (also known as Procion Yellow H-E3G),

Size of Dyer	Type of Treatment	Initial Infrastructure Cost (USD)	Cost per Liter Treatment (USD)	Liters per Day to be Treated in System	Daily Cost (USD)	Effluent Content	Treatment Level (Complete or Pretreatment)
Large-scale [Personal Discussions]	2 settling tanks, and 2 reverse osmosis units	NA	0.005	3,000,000	15,000	Zero-discharge, easily reuseable for new dye batches	Complete
Medium-scale [Personal Discussions]	Settling tanks, biodegradation, sand/carbon filtration, drying beds	30,000	0.003-0.005	40,000	133-200	Permissible levels of organics and inorganics for industrial disposal	Complete
Small-scale [Preliminary Small-Scale System]	Sustainable photo-Fenton Oxidation Rusty container and Cotton/Sand/Carbon Filtration Unit	50	0.026	1,000	26	High conductivity, safer for dumping compared with untreated but requires reverse osmosis for complete treatment	Pretreatment

Table 1: Comparison of infrastructure and treatment costs of large and medium dyers compared with the sustainable photo-Fenton oxidation and filtration method for small-scale dyers.

Dye Type	Dye Color	Iron Quantity	6% Hydrogen Peroxide Volume (mL)
Reactive	Red	Low	250
Reactive	Red	Medium	150
Reactive	Red	High	100
Reactive	Yellow	Low	250
Reactive	Yellow	Medium	150
Reactive	Yellow	High	100
Reactive	Blue	Low	500
Reactive	Blue	Medium	300
Reactive	Blue	High	200

Table 2: Amount of 6% hydrogen peroxide used with various dye colors, types, and amounts of rusty iron.

Oxidation Time Filtration Type		Iron Surface Area	Abbreviation
(Full or Partial)		(High, Medium, Low)	
Full	None	High	R1H
Full	Sand	High	R2H
Full	Sand and Carbon	High	R3H
Partial	None	High	R4H
Partial	Sand	High	R5H
Partial	Sand and Carbon	High	R6H
Full	None	Medium	R1M
Full	Sand	Medium	R2M
Full	Sand and Carbon	Medium	R3M
Partial	None	Medium	R4M
Partial	Sand	Medium	R5M
Partial	Sand and Carbon	Medium	R6M
Full	None	Low	R1L
Full	Sand	Low	R2L
Full	Sand and Carbon	Low	R3L
Partial	None	Low	R4L
Partial	Sand	Low	R5L
Partial	Sand and Carbon	Low	R6L

Note: If iron surface area is not taken into account, the notation R1*-R6* will be used.

Table 3a: Abbreviations of sample names for experiments.

Oxidation Time (t _o or Full)	Added Chemicals (None, HCl, HCl and H ₂ O ₂)	Abbreviation		
to	None	C1		
t	HCI	C2		
t	HCI and H ₂ O ₂	C3		
t _F Full	HCI	C4		
t _F Full	HCI and H ₂ O ₂	C5		
Note: Control samples used no filtration.				

Table 3b: Abbreviations of control sample names.

and Blue 4 for analysis of the performance of the treatment process. Other factors in favor of their use include ease of procurement and the ability to compare with other dye oxidation studies. Molecular masses of these dyes are 1469.98 g/gmol, 1632.18 g/gmol and 637.43 g/gmol, respectively, while their CAS numbers were 61951-82-4, 59112-78-6 and 13324-20-4, respectively. Normal tested or documented wavelengths of these dyes are at 535 nm for Red 120 [12], documented maximum wavelength of Yellow 81 were 270 nm and second at 356 nm [13] and finally, that of Blue 4 was at 595 nm [14].

The Linear chemical formulae of these dyes are $C_{44}H_{24}Cl_2N_{14}O_{20}S_6Na_6$, $C_{52}H_{34}Cl_2N_{18}Na_6O_{20}S_6$, and $C_{23}H_{14}Cl_2N_6O_8S_2$, respectively, while their chemical structures are shown schematically in Schemes 1a-1c.

Water, acid, and oxidant: Tap water was used to dissolve all dyes. Since water quality varies throughout the world and the difference between the water quality in the USA and India and within India (irrespective of a rural community or a city) alters dye samples with enough variability, one could expect large variations in the results obtained.

Hydrochloric acid (HCl) of approximately 1M was chosen as the acidifier to bring the dye solution to a pH of 2.5-3.0. HCl was used due to its ready availability throughout India. It is well known that HCl can react with the oxidation chemicals and the dye intermediates thus producing some unwanted byproducts such as chlorides. Sodium levels are often high in treated dye effluence because of the strong attraction between chloride and sodium ions, creating sodium chloride. Sodium chloride is very soluble in water and will remain in solution even after filtration. Although chloride levels from HCl are high, possible byproducts resulting from acidification using other acids are much more obtrusive.





Scheme 1b: Reactive Yellow 81 (Procion Yellow H-E3G) chemical composition (World Dye Variety, 2012).



Hydrogen peroxide was used as an oxidizer in the photo-Fenton process in the present study. A 6% solution, which is 1.76 M, was used due to its low cost and availability to small-scale dyers. Table 2 shows the amount of 6% hydrogen peroxide used with various dye colors and amounts of rusty iron.

Sand and carbon filters: A sand filter for the 1-liter experiments carried out in the present study was made of readily-available construction sand from the area and required approximately 0.5 m depth of sand with a diameter of 40 cm. In the case of the laboratory experiments in the USA, the fully oxidized samples were first filtered, followed by the partially oxidized sample; after this, the sand was changed. The reason for this is because un-oxidized dye color permanently dyes the sand in the filter and cannot be removed without using excessive amounts of water.

Further, activated carbon was used after sand filtration with the expectation that it will adsorb any residual color or chemical intermediate in solution after oxidation and sand filtration. The carbon filter was rinsed twice between filtration of different samples.

Following one of the philosophies of the present study that the process developed for the treatment of effluent of dyes to be economical, activated carbon was initially used in the laboratory experiments, although one may think of using wood charcoal instead of more expensive activated carbon in future studies for the field experiments.

Methods

By mimicking the cottage-scale silk dyers' wastewater in laboratory-scale studies, the intent was to augment dyers' processes with a low-cost treatment option. For this reason, the following experimental methodology was chosen. (1) Reactive Dyes at 5 g/L concentration were mixed with household hydrochloric acid (Lion Brand toilet bowl cleaner cost 0.80 USD per 1-L). (2) 6% Pharmacygrade hydrogen peroxide (0.37 USD per 100 mL) was poured into the solution in containers holding rusty metal from old yogurt containers (free as they were found in dump). (3) Natural sunlight at ambient temperature was employed. (4) Following treatment, sand and carbon filtration of the dye effluent was used (container cost minimal may be found in dump, sand found in local environment). Cost is limited to chemical consumption and ranges per liter dye effluent from 0.37-1.84 USD for peroxide and is minimal for acid at approximately 0.01 USD for 10 mL/L, totaling 0.38-1.85 USD per liter. Although this is significantly higher than the cost of effluent treatment for a largescale dyer mentioned previously and detailed in Table 1 (0.005 USD per L), the infrastructure for the sustainable photo-Fenton oxidation and filtration method here uses recycled scrap materials with minimal costs as compared to the expensive reverse osmosis and biological and chemical settling tanks at the large-scale operation.

Photo-Fenton oxidation studies: It is known that variables that affect the photo-Fenton oxidation process are the (i) UV light source (sunlight angle in India or the USA), (ii) color of dye (red, yellow, or blue), (iii) water source for mixing dyes, (iv) acid used to bring pH to 2.5-3.0 (here hydrochloric acid is used) (a pH increase of 1 generally occurs during oxidation, all samples require filtration to separate sludge from liquid, and sand raises pH further as is noted later), (v) hydrogen peroxide volume added as the main oxidizing agent, (vi) surface area of rusty iron pieces as the chemical catalyst (high, medium, low), (vii) time (partial or full oxidation), and (viii) filtration (none, sand, or sand and carbon). Accordingly, photo-Fenton research was carried out using direct sunlight during the summer/fall months in

Reactor: Considering the outcome of this study was intended to function in small-scale cottage industry silk dyers, a reactor was fitted with rusty metal sheets cut from the sides of old yogurt containers found in an open dumping site in India, where 50% of the studies were performed. As this work was intended to function for small-scale cottage industry silk dyers, the materials (the rusty metal and sand) used were as found in the field.

In order to optimize the time to stop the photo-Fenton oxidation reaction, experiments were carried out by taking a 5 mL sample every 5 minutes during oxidation, adding 1 drop of 0.1M sodium hydroxide to raise the pH above neutral (9 for Reactive Red 120, 9.37 for Reactive Yellow 81, and 8.86 for Reactive Blue 4). The undiluted samples were then analyzed using UV-visible spectrometry to find the time when the color became partially degraded by watching the peak height of the color and any organics left in solution decrease with increased oxidation time. Full oxidation time was chosen when all peaks on the spectral analysis decreased to zero. Partial oxidation time was chosen when the peaks on the spectral analysis were visibly separated from each other and could each be identified as an individual chemical peak.

All the samples listed in Table 3a were then tested for the three dye colors (red, yellow, and blue) after experiencing three filtration methods (none, sand, sand and carbon), Table 3b lists the control samples.

Measurements: UV-visible spectrometry was used as an analysis method to determine the optimal time for partial and full oxidation for the reactive dyes using photo-Fenton oxidation after optimizing hydrogen peroxide quantity much like other studies [4,5,7,16,17]. In addition, with a view to monitoring the color changes and also peaks of color intensity, an HP 8453 Agilent UV-visible scanning spectrophotometer was used with scans from 190-1100 nm wavelengths in 10 mm quartz cuvettes. Experiments on each dye yielded peak absorbance at particular wavelengths.

Broad organic chemical levels present in the water samples were carried out through COD as an indirect measurement of the amount of organic compounds present in a solution similar to other studies [18]. This was measured colorimetrically using a Hach Meter 890. Samples were digested at 148°C for 120 minutes with one sample of de-ionized water as a control. The digested samples were then measured at 600 nm colorimetrically with the control as zero to measure the color change relative to water.

GC/MS analysis was used to measure (qualitative analysis) and label organic chemical intermediates found in solution just as other studies [17,19,20] before and after oxidation as well as after filtration. For this purpose, Solid-phase Micro Extraction Coupled with Gas Chromatography/Mass Spectrometry (SPME-GC/MS) was used. First the samples were extracted using Solid Phase Micro-Extraction (SPME) with a 65-µm Polydimethylsiloxane/Divinylbenzene (PDMS/ DVB), Stableflex 24Ga fiber assembly (Supelco) controlled by a manual Micro-Extractor holder immersed in each sample for a minimum of 50 minutes. A 65-µm PDMS/DVB partially polar fiber is typically used for amines and nitro-aromatic compounds with molecular weights between 50-300 g·mol⁻¹. This fiber was chosen since the oxidation of dyes typically results in the formation of amines. After the extraction was complete, the fiber was injected into a GC System Hewlett Packard,

HP 6890 Series, MS Agilent Technologies Mass Selective Detector 5973 Network and column HP-5MS (Crosslinked 5% PH ME Siloxane) with 30 m x 0.25 mm, 0.25 µm film thickness (Hewlett Packard Special Performance Capillary Column). Maximum injector volume was 1.0 µl with an inlet heat of 250°C and a pressure of about 52 kPa; total flow was 103 mL/min and split ratio of 100:1 with flow of 99.5 mL/min and an average velocity of 36 cm/s. Helium was used as the carrier gas at a flow-rate of 103 mL/min at a pressure of 52 kPa. The oven was set for an initial hold at 50°C for 5 min, followed by a ramp-up of 10°C/min until a temperature of 160°C was reached. Then, there was a hold for 2 min, followed by a ramp-up of 5°C/min until 235°C was reached. This was followed by a hold for 17 min for a total run-time of 50 minutes. The maximum temperature of the column was 300°C. The detector heat was set at 150°C, hydrogen gas flow set at 40 mL per minute and air at 450 mL per min. Analysis of samples was completed by the attached mass spectrometer connected with NBS75K.L library.

With a view to qualify the chemical peaks detected by the GC, they must reach a minimum of 10,000 abundance (based on the electrical signal passed through the sample) and match the MS library with 80% or more accuracy. In order to verify the quantification of abundance of organics found in solution, a 95% pure sample of Tolylene, 2,4-diisocyanate (also called Benzene, 2,4-diisocyanato-1-methyl, one of the aromatic and cyanate chemicals found in solution after treatment) was tested using the same GC/MS methods listed above.

Identification of metals and their quantity left in solution was analyzed using an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) as this technique has been normally used for the determination of metals and ions in order to quantify and qualify the levels of metal ions left in solution after the following tests: (1) photo-Fenton oxidation, (2) photo-Fenton oxidation followed by sand filtration, and (3) photo-Fenton oxidation followed by sand and carbon filtration (both fully and partially oxidized).

The test methods followed in this study were similar to previous reports [21-23]. Under the standard methods for the examination of water and wastewater [24] all results were determined in filtered and acidified samples and the flowing stream of argon gas was ionized by applied radio frequency field ~27.1 MHz. The Instrument Parameters of ICP used were 1.00 kW power, 15 L/min of plasma, 200 kPa of Nebulizer pressure, argon gas flow of 1.5 L/min with viewing height of 10 mm, pump rate of 15 rpm and Spectrometer Atomic Emission Spectroscopic studies having a photodiode array with dwell time of 30 sec.

Finally, scrap sheet iron used was characterized according to surface area as it is believed that the iron that acts as a catalyst in the photo-Fenton oxidation reaction acts at the interface between UV light and iron. For 1-liter solutions, low iron was 165 cm², medium iron was 323 cm², and high iron was 645 cm². This measurement differs from other studies that use scrap metal that measured iron quantity by volume or weight [19,25-27].

Sludge that is produced during the photo-Fenton oxidation process included both organic dye and inorganic iron as described in review reports [28]. ICP-AES measured quantities of iron in control samples and treated samples. For the Indian samples, iron and dye sludge was quantified volumetrically. In brief, one-liter solution was poured into a volumetric cylinder and allowed to settle overnight. A measurement was then taken of the foam that rose to the top as well as the sludge that settled to the bottom of the solution.

Respirometric analysis: To determine the biodegradable quality

of the residual solution, respirometric analysis was performed as in a previous publication [29]. Biodegradability of solution is an important factor to test as can be seen in previous reports [7]. For this, the sludge from a local Common Effluent Treatment Plant (CETP) in India was used as biomass for this analysis. This allowed for the determination of whether the sludge from a CETP can uptake oxygen in the presence of the contaminants left in the photo-Fenton oxidized samples. Oxygen released due to consumption of the pollutant given to the bacteria was measured in the digital oxygen system (Model 10, Rank Brothers, Bottisham UK) instrument.

Scanning electron microscopy (SEM): To determine whether there were any other impurities in solution affecting the oxidation process and to ensure that the ferrous ions in the rust were in fact working as catalyst for the photo-Fenton oxidation process, surface content of iron pieces was measured using SEM (Hitachi S-4800) much like other works using SEM for photo-Fenton oxidation studies [4,5,22,30]. This also had an attachment of 15 mm Energy Dispersive X-ray Spectrometer (EDX) with a detector distance of 1.5 mm for elements analysis used to map various elements (Fe, Cl, S, Al, Fe, O, C).

Statistical analysis: Considering the number of variables used in this study, to determine the main effects and the interaction effects due to three factors: color (red, yellow, or blue), quantity of iron (low, medium, or high), and time (t_o , partial oxidation time, full oxidation time), the biological variable (biodegradability based on bacteria's oxygen uptake) was treated as dependent and was analyzed using three-way analysis of variance [31]. ANOVA was performed with a full model separately for all the three variables similar to that reported earlier [32]. For each combination of factors, the dependent variable data was available in triplicate, resulting in a balanced factorial design.

Results and Discussions

Scanning electron microscopy study

Figure 1 shows scanning electron micrograph of the iron rust from the scrap iron material at 1.5K, found to be composed of Fe, S, Al, and C as determined by EDAX (not shown). It can be seen from Figure 1 that the surface morphology of the iron rust is an uneven surface with different sizes (submicron) of rust spread all over the surface. Similar observations of surfaces of different materials used in photo-Fenton studies have been observed by other researchers [4,5,22,30,33].

UV-visible spectrometry results

Peak absorbance yielded on each dye at particular wavelengths is listed in Table 4. It may be noted that the present values found have previously been reported as phenol and benzene in other studies. For example phenol values reported are 209 nm, 269 nm [34]; while those



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Dye	Phenol (nm)	Benzene (nm)	Color Wavelengths (nm)	Unknown Peaks Found (nm)
Reactive Red 120	206	237	536	291, 371, 512
Reactive Yellow 81	206	229, 243	268, 352	410, 520
Reactive Blue 4	206	230, 258	597	369, 520

Table 4: Peak absorbance wavelengths for the tested dyes and their likely responsible chemicals.

of benzene reported are 235 nm [35], 226 nm [18], 230 nm [36], and 260 nm [16]. However, naphthalene was not found in the present treated samples contrary to those reported in other studies such as at 315 nm [36], and at 318 nm [18]. On the other hand, color wavelength has been confirmed by the present study while unknown peaks reported in the present study have not been reported by others.

Rate reaction: Spectra obtained by UV-visible spectrometry for Reactive Dyes (Undiluted C1, R1H, and R4H spectra of Reactive Red 120, Reactive Yellow 81, and Reactive Blue 4) using photo-Fenton oxidation after optimizing hydrogen peroxide quantity are shown in Figure 2 displaying the unmodified spectra peak heights for t_o, partial, and full oxidation samples C1, R1L, and R4L spectra of the three Reactive Dye colors for low iron (high and medium iron trend is similar). Generally, UV and visible peaks for t_o are beyond the 4.0 maximum thus denoting the need for decolorization and degradation. It can also be seen that visible peaks of partial oxidation have decreased to within the 4.0 scale and display clear peaks that can be described as individual organic chemicals. On the other hand, full oxidation samples displayed peaks at a lower UV range and no peaks in the visible range meaning that full oxidation time was chosen when complete decolorization had occurred. The actual control peak heights C1-C5 are calculated from dilutions for Reactive Red 120, Reactive Yellow 81, and Reactive Blue 4 respectively. Table 5 lists the partial and full oxidation times chosen from Figure 2 for the three Reactive Dye colors using different iron surface areas.

Partial and full oxidation results: Figure 3 compares spectra of Reactive Red 120 dye (a) R1H-R3H, (b) R4H-R6H, (c) R1M-R3M, (d) R4M-R6M, (e) R1L-R3L, (f) R4L-R6L with that of the diluted control peak C1. Similar spectra were obtained for Reactive Yellow 81 and Reactive Blue 4 dyes. These are not included as there will be too many figures in the paper.

In Figure 3, peaks found at 206 nm were only present after acid and hydrogen peroxide were added to solution (C2-C5 not shown). Peaks at 237 nm, 291 nm, 371 nm, 512 nm, and 536 nm were also visible in C1. In general and despite treatment, the peak at 206 nm stayed much higher than the other pollutants in solution. The contaminants displaying UV peaks at 206 nm, 237 nm, 291 nm, 371 nm were reduced most by full oxidation. Sand and carbon filtration following oxidation greatly decreased the height of the peaks by physically removing the organics out of solution. The greatest impact of iron on peak degradation occurred for medium iron. The contaminants displaying visible peaks at 512 nm and 536 nm degraded more by partial oxidation than by full oxidation consistently for all iron levels. However, sand and carbon filtration following full oxidation was more effective at removing the chemicals responsible for peaks at 512 nm and 536 nm (thus making full oxidation followed by sand alone or sand and carbon the most effective treatment). The medium iron level was still the most effective for removal of these organics. As with the UV wavelength peaks, generally sand filtration accomplished more than the carbon filter due to physical capturing of the solids created by the photo-Fenton oxidation process and physically removing them from solution, although carbon filtration did no harm to the process.

Dye	Iron Quantity	t₀ (min.)	t _{partial} (min.)	t _{Full} (min.)
Reactive Red 120	High	0	40	60
Reactive Red 120	Medium	0	55	75
Reactive Red 120	Low	0	75	135
Reactive Yellow 81	High	0	35	70
Reactive Yellow 81	Medium	0	85	155
Reactive Yellow 81	Low	0	75	135
Reactive Blue 4	High	0	100	125
Reactive Blue 4	Medium	0	155	180
Reactive Blue 4	Low	0	180	220

Table 5: Partial and full oxidation times for Reactive Dyes.

In the case of Reactive Yellow 81 peaks were found at 206 nm, 229 nm, 243 nm, and 520 nm in C2-C5 only after acid and hydrogen peroxide were added to solution. Peaks at 268 nm, 352 nm, and 410 nm were also found in C1. Just as with Reactive Red 120, the peak at 206 nm remained after treatment. In addition, the peak at 229 nm stayed much higher than the other peaks despite treatment. The contaminants that displayed UV peaks at 206 nm, 229 nm, 243 nm, 268 nm were reduced the most from full oxidation compared to partial oxidation. Sand and carbon filtration following oxidation greatly decreased the heights of the peaks by physically removing the organics out of solution. In general, medium iron had the greatest impact on the degradation of these peaks.

The contaminants displaying peaks at 352 nm, and 410 nm exhibited behavior similar to both the UV and visible peaks of Reactive Red 120. Partial oxidation decreased peak height to below full oxidation samples; however, sand and carbon filtration raised the levels again. Full oxidation followed by sand and carbon decreased the levels to near negligible. Medium iron gave the lowest numbers, however the same samples using low and high iron were similar.

The contaminants displaying a visible peak at 520 nm was reduced most from full oxidation followed by sand and carbon filtration. Unlike all other dyes tested, low iron levels removed pollutants from the treated Reactive Yellow 81 solution the most, closely followed by medium and then high iron.

In the case of Reactive Blue 4 dye, peaks were found at 206 nm, and 520 nm only after acid and hydrogen peroxide were added to solution (C2-C5), while peaks at 230 nm, 258 nm, 369 nm, and 597 nm were also found in C1. Just as with Reactive Red 120 and Reactive Yellow 81, peaks of the UV spectra of Reactive blue4 dye at 206 nm, 230 nm, and 258 nm remained much higher than the visible peaks despite treatment. Degradation of the contaminants displaying these UV peaks occurred most after full oxidation using high iron followed by sand and carbon filtration.

The contaminants displaying peaks at 369 nm, 520 nm, and 597 nm presented a mixture of results. The greatest degradation was still with high iron, followed closely by low iron and medium iron.

It may be noted that all the results obtained in UV-visible spectrometry can be compared with published data [16,18,34-36] to describe which organics were left after treatment. Further, as will be

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seen later, observed UV-visible spectrometry results are comparable with those observed in the COD studies in respect to total organic load remaining. Generally, full oxidation followed by sand and carbon filtration was most effective for red, yellow, and blue dye removal; while optimal iron level cannot be determined as peaks lowered differently with changes in iron surface area.

COD results

COD levels in the present study showed great variability, even when comparing similar samples. This may be due to the fact that the high level of dye used in this study has an exceptional level of organic material. Photo-Fenton oxidation also forms sludge in solution that is comprised of dye and rust from the iron catalyst. For this reason COD levels that dropped below the Karnataka State Pollution Control Board's (KSPCB) allowable 250 ppm are particularly to be noted. In the analysis of the data, it is important to also consider ambient temperature, sunlight, and pH during the experiment in order to capture the effects of these variables on the COD reduction caused by the photo-Fenton oxidation process.

COD results related to the three reactive dyes with respect to temperature, pH, iron, and sunlight were compiled. Figure 4a-4c depicts the COD results comparing C1 to R1H-R6H, R1M-R6M, and R1L-R6L in both India and the USA for Reactive Yellow 81 (trend for Reactive Red 120 and Reactive Blue 4 similar). In general, a decrease of COD from C1 to R4*, R1*, R5*, R6*, R2*, R3* for the respective surface areas of iron in solution is observed.

The control samples for Reactive Red 120 had COD levels that ranged between 2392 and 7320 ppm. Full oxidation using medium iron followed by sand filtration lowered COD levels to a greater extent and this agrees with the UV-visible spectrometry results. COD decreased well below the permissible effluent levels using full oxidation followed by filtration despite iron surface area. From highest to lowest, the COD value trends, regardless of iron differences, are R4*, R1*, R5*, R6*, R2*, R3*. The fully oxidized samples produced more sludge than the partially oxidized samples. Sludge kept the COD higher than permissible effluent levels; however, after physical removal of the sludge using sand and carbon filtration, the COD was lowered close to negligible. Since partial oxidation does not fully precipitate the organics out of solution (and thus creates less sludge), the sand and carbon filtration cannot fully separate them from the water base which results in a higher COD. The low iron sample in India did not exactly follow the same trend since full oxidation brought the COD to permissible effluent levels and much lower than the partially oxidized sand and carbon filtered samples.

COD levels ranged between 2070 and 9760 ppm, in the case of Reactive Yellow 81, while the control samples had ranged between 2262 and 7240 ppm. As in the case of Reactive Red 120 dye, in the case of these two dyes also, full oxidation using medium iron followed by sand filtration lowered COD levels to a greater extent. This agreed with the UV-visible spectrometry results for both these dyes. Also, COD values decreased well below the allowable effluent levels using full oxidation followed by filtration, independent of the iron surface area in both the cases of dyes. Similarly, from highest to lowest, the COD value trends were the same as Reactive Red 120. The trend is independent of iron level and the location of the study. However, it may be noted that while the trends were consistent, the individual numbers could differ greatly between repeated experiment samples.

The control samples for Reactive Blue 4 had COD levels that ranged between 2262 and 7240 ppm. Full oxidation using medium iron

followed by sand filtration lowered COD levels the most. This agrees with the UV-visible spectrometry results. COD decreased well below the allowable effluent levels using full oxidation followed by filtration, independent of the iron surface area.

The fully oxidized samples produced sludge that kept the COD higher than permissible effluent levels. However, after physical removal of these organics, the sand and carbon filtered samples brought COD close to negligible. Since partial oxidation does not fully precipitate the organics out of solution, the sand and carbon filtration cannot fully separate them from the water base, these resulted in a higher COD values. The high iron sample in India did not follow this same trend, but the fully oxidized and filtered samples had higher COD than the partially oxidized and filtered samples. High COD levels were found in control samples due to the high concentration of dye in solution.

Sludge production

The percentage sludge production using sustainable photo-Fenton oxidation was expected and discussed in previous reports [28], and was found in this study to be low. Sludge production was notable during the photo-Fenton oxidation process with more sludge being produced for longer duration experiments. Sludge volume was quantified during the India studies and percent volume sludge per 1-liter laboratory tests for each dye color after full oxidation are as follows.

Reactive Red 120 dye gave about 0.97% with high iron, 6.7% with medium iron and about 6.5% for low iron. Values of these for Yellow 81 and Reactive Blue 4 dyes are about, 0.96% and 3.3% (high iron), about 7.3% and 4.3% (medium iron) and about 3.3% and 5.4% respectively. It can be seen from the above values that high iron surface area produced the least amount of sludge, followed by low iron, and then medium iron. Since sludge was removed from solution using filtration, presence of sludge in non-filtered samples could greatly impact the overall COD level. It was learned that sludge production created from biodegradation (customary method of dye effluent treatment in medium and large-scale textile plants) of their wastewater, was approximately 15% of total solution [Personal Communications].

Effect of solar irradiance and temperature

Generally, the solar irradiance in the USA tests was higher (383-720 W/m²) than solar irradiance tests in India (81-485 W/m²), since studies in India were completed at the beginning of the rainy season. While the USA tests were completed at lower ambient temperatures (0.41-23.9°C), India tests were performed during the period when the temperature was in the range of 25.6-28.9°C. Decolorization and degradation occurred for both test sites, indicating that the process can work for a wide range of temperatures and solar irradiances. COD levels varied more as a result of time and filtration rather than solar irradiance and temperature. The COD levels that resulted from the extreme ends of solar irradiance or temperature were mid-range COD results. It can therefore be concluded that while UV irradiance and temperature are important parts of the chemical reaction, without which the reaction could not take place, they are not the key factors in the success of the study. The tests were successful despite the lack of direct sunlight in overcast or partly sunny conditions as long as there was daylight. This is important for eventual field implementation of the process, as both solar irradiance and temperature are variables that cannot be easily controlled in practice.

GC/MS results

The GC/MS graph of the control is shown in Figure 5. This 95%

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pure sample absorbed onto the Solid Phase Micro-Extraction (SPME) fiber was found to have an abundance of Benzene, 2,4-diisocyanato-1-methyl at 1,800,000, as well as Dodecanoic Acid, Ethyl Ester at 28,000; 2H-Benzimidazol-2-one, 1,3-dihydro-5-methyl at 100,000; 2-Propenoic acid, 3-(4-methoxyphenyl)-,2-ethylhexyl ester at 40,000; Bis(2-ethylhexyl) phthalate at 95,000 and squalene at 50,000. This verifies the lesser relative abundance found in samples tested using SPME and GC/MS.

Results obtained for Reactive Red 120 can be found in Supplementary Table S.1, which gives an overview of GC/MS results of all chemicals found in C1-C5, R1H-R6H, R1M-R6M, and R1L-R6L for Reactive Red 120 and what type of compound each result is and their responsible functional groups including when complete degradation had occurred (which resulted in no noticeable peaks). Similar results were obtained in the case of the other two dyes (Reactive Yellow 81 and Reactive Blue 4). From Supplementary Table S.1, it becomes evident that various organic compounds were left in solution after treatment, but with decreasing abundance as was observed for all dyes.

In the case of Reactive Red 120 dye, aromatics in control samples measured at very high levels while combined compounds were lower. Due to chemical alteration during oxidation, treated samples showed higher abundance of only combined compounds. In the case of Reactive Red 120, mostly aromatic and alcohols, and aromatic and cyanate combined compounds with less aromatic and ether and aromatic and aldehyde combined compounds were present. Percent remaining in treated samples was taken from total compounds remaining in USA C1 compared with treated samples. USA sample R1L decreased to 4.3% of original while R4L to 2.9%, and R5H to 3.6%. India samples R2H decreased to 3.7% of original, R2M to 0.9%, R2L to 2.6%, R3H to 3.5%, R4H to 1.0%, R5H to 3.7%, and R6H to 5.9%. All other samples showed no remaining compounds in solution using GC/MS after treatment. Similarly for Reactive Yellow 81 most samples decreased completely while few remained that included mostly aromatic and alcohol combined compounds, aromatic and cyanate combined compounds, with less aromatic and aldehyde combined compounds, and amine combined compounds, aromatic, azine, and chloride combined compounds, and finally aromatic, chloride, and imino combined compounds with slightly higher percentages for India samples R2M and R3H.

In the case of Reactive Blue 4, C1 had undetectable levels of organics in solution possibly due to its different dye chemical composition. C3 however due to its lower pH and its peroxide level was found to contain aromatics, ketones, azines, amines, and chlorides and therefore was used for the control comparison. As with Reactive Red 120 and Reactive Yellow 81, the majority of treated samples were found to contain no detectable organics. However for Reactive Blue 4, R1H in the USA and R4H in India were found to contain higher levels of organics after treatment. Other samples such as R5H in India, and R4H and R4M in the USA were found to decrease only 24-47% of C3.

From the GC/MS graphs obtained it became evident that control samples had the most detectable organic chemicals found in solution in the case of all the dyes. For example, Figure 6a displays Reactive Yellow 81 C1 while Figure 6b shows Reactive Yellow 81 R1H with much lower peaks. Similar graphs were obtained for Reactive Red 120 and Reactive Blue 4 dyes controls compared with treated samples. In the case of Reactive Red 120 dye treated samples, fully oxidized samples degraded more than partially oxidized samples. Medium iron samples had the least amount of organics as found from GC/MS analysis. India samples had many more organics in solution than USA samples. Full

oxidation using medium iron followed by sand filtration in the USA revealed the least amount of chemicals (carbon samples were not tested if sand filtered samples found no chemicals).

Although C1 had the most detectable organic chemicals found in solution in the case of Reactive Yellow 81 dyes, treated samples, partially oxidized samples degraded more than fully oxidized samples. Low iron samples had the least amount of organics as indicated by GC/ MS measurements. India samples had many more organics in solution than USA samples. Medium iron oxidized samples in the USA returned no organics in solution.

Unlike Reactive Red 120 and Reactive Yellow 81, C4 for Reactive Blue 4 had the most detectable organic chemicals found in solution. This means that after acidifying the solution and leaving it to react with neither oxidant nor iron catalyst in the sun, more organic compounds were found in solution. Just as with Reactive Yellow 81 samples, low iron samples had slightly less chemicals in solution than medium iron. USA samples had many more organics than India samples. Medium iron oxidized samples in the USA or India returned no organics in solution.

ICP results

Figure 7 shows ICP results testing for iron, calcium, and magnesium from Reactive Red 120 dye samples both in India and USA. It can be seen from Figure 7 that iron always decreased below permissible levels after filtration; calcium and magnesium were always below the permissible limits. In the case of USA samples, sand influenced calcium levels, while sodium was never below the permissible limits in neither USA nor India samples.

Although 18 metals were measured, only four were found regularly at high levels: calcium, iron, magnesium, and sodium. Their levels were measured for all samples from C1-C5, R1H-R6H, R1M-R6M, and R1L-R6L to track when levels decreased below permissible limits. Arsenic, cadmium, lead, and manganese were occasionally found above permissible limits and it could be noticed when this occurred. Data were taken for all the samples, including from the tests carried out both in India and USA. India's available permissible effluent standards for wastewater in Dye and Dye Intermediate Industries for disposal in surface waters do not list calcium, iron, magnesium, and sodium in their effluent regulations [37]. Therefore, levels of these observed metals were compared to global permissible drinking water standards [37-39]. Permissible calcium levels are limited to 75-200 mg/L because calcium causes water hardness between 40-100 mg/L, while the permissible magnesium levels are limited to 30-150 mg/L in view of the taste of the water being affected at 500 mg/L. Similarly, in the case of iron, permissible levels are limited to 0.1-1.0 mg/L because of the taste and aesthetics of the water being affected at 0.3 mg/L. On the other hand, permissible sodium levels are limited to 20 mg/L because, (i), sodium levels in natural water is between 5-50 mg/L and (ii) at 250 mg/L the taste and aesthetics of natural water is affected and can alter natural biological activity. Similarly, permissible manganese levels are limited to 0.1-0.5 mg/L, but at 0.05 mg/L the taste and aesthetics of the water are affected. In the case of metals such as arsenic, cadmium and lead, which affect human health, permissible levels are 0.01-0.05 mg/L, 0.005-0.01 mg/L and 0.05-0.1 mg/L respectively. This is because, at 0.05 mg/L arsenic affects human health; cadmium at 0.005 mg/L is toxic to humans, while lead causes irreversible neurological damage to humans, especially children [40,41].

The general trend of these ions in obtained solution in this study



Figure 7: ICP Results both in (a) India and (b) USA including iron, calcium, and magnesium for Reactive Red 120 dye.

(a)			
Sample	Amount of Fe	No Filter/Filter	O ₂ Uptake (nmol/min/mg)
R4H	High	No Filter	3.84
R5H	High	Sand Filter	0.00
R4M	Medium	No Filter	40.6
R5M	Medium	Sand Filter	75.4
R4L	Low	No Filter	0.00
R5L	Low	Sand Filter	0.00
(b)			
Sample	Amount of Fe	No Filter/Filter	O ₂ Uptake (nmol/min/mg)
R4H	High	No Filter	1.58
R5H	High	Sand Filter	0.00
R4M	Medium	No Filter	365
R5M	Medium	Sand Filter	2.33
R4L	Low	No Filter	0.00
R5L	Low	Sand Filter	101
(C)			
Sample	Amount of Fe	No Filter/Filter	O2 Uptake (nmol/min/mg)
R4H	High	No Filter	0.00
R5H	High	Sand Filter	0.00
R4M	Medium	No Filter	7.36
R5M	Medium	Sand Filter	620
R4L	Low	No Filter	0.00
R5L	Low	Sand Filter	0.00

Table 6: Calculated oxygen uptake according to low, medium, or high iron and non-filtered or sand filtered sample results for (a) Reactive Red 120; (b) Reactive Yellow 81; (c) Reactive Blue 4.

was an increase of calcium and magnesium after sand filtration. Iron had the opposite trend, as it increased during the oxidation process and decreased to an almost negligible amount after sand filtration. This was a result of the physical capturing of the iron/dye sludge formed in solution during the oxidation process. Sodium increased or remained stable during oxidation and decreased after sand and carbon filtration. It may be noted that the levels of increase or decrease do not fit any mathematical trend, because of the variability in chemical composition of the wastewater at such a high dye concentration. In addition, there was little control over the contents of Indian sand, since it was used for construction and had been stored outside and open to nature, prior to use. Because of the difference in quantitative results between India and the USA, only the trends are described. These trends often matched despite these numerical differences. These trends were often comparable despite varying iron surface areas described in this study as well differing locations of testing (India and USA). Considering that similar results were found for the three dyes, for the sake of brevity, only Reactive Red 120 results are described here.

For example, in the case of Reactive Red 120 dyes, it was observed that all ICP results were within the drinking water permissible limits for calcium (below 200 mg/L) and magnesium (below 150 mg/L). Further, other than calcium, magnesium, iron, and sodium, manganese was also present occasionally in the India samples, but only after sand or carbon filtration was performed. Most India filtered samples showed a level of manganese in solution (except R2H, R2L-R3L), along with the presence of arsenic in R3H. On the other hand, USA samples

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(particularly R1H, R4H, R1M, R1L, R3L, and R5L) showed at times, low but varying levels of manganese, lead, and arsenic than those of Indian samples, and typically after no filtration.

Calcium controls ranged from 20 to 37 ppm with the highest level in C1, magnesium ranged from 7 to 14 ppm with the highest level in C1, iron from 0.1 to 4 ppm with the highest level in C4-C5, and sodium from 580 to 1100 ppm with the highest level in C4. Similarly, calcium and magnesium content in solution changed as iron surface area and location of test changed. For high iron, fully oxidized Indian samples had more metals than partially oxidized samples, while those of USA samples had fewer metals than partially oxidized samples. However, all of these samples increased with filtration.

On the other hand, for medium iron, partially oxidized samples had more metals than fully oxidized samples in the case of both Indian and USA samples. However, iron in all of these samples increased with filtration except for USA samples, opposite results were observed for R2M-R3M samples. Finally, for low iron, fully oxidized samples had more metals than partially oxidized samples. Here also, all the samples increased with filtration except USA samples R2M-R3M.

Similarly, iron concentration in solution changed as iron surface area and location of test changed. Longer oxidation time resulted in higher iron metal content for non-filtered samples, while filtration resulted in lower iron content especially after full oxidation (except India samples R5L-R6L). Medium, low, and high iron surface area resulted in less metal in solution respectively for all samples. One exception is for India samples R5L-R6L having a larger metal content than R4L. Samples R2H, R3H, R2M, R3M, R2L, and R3L showed iron content below the permissible limits. However, samples R6H, and R6M also showed below the permissible limits, although 3-10 times higher than the fully oxidized equivalents.

For sodium, none of the samples decreased to below permissible limits except R6H in India, and R2M and R3M in the USA. On the other hand, samples R2H-R3H, R2M-R3M, and R2L-R3L (except R2H and R3H in India) showed lower level than R5H-R6H, R5M-R6M, and R5L-R6L. Generally, it was observed that more sodium was removed from solution with more filtration. Low, medium, and high iron surface area resulted in less metal in solution respectively for all samples.

Respirometric results

Since COD values of fully oxidized samples were too low to biodegrade further, respirometric analysis was carried out only for partially oxidized samples of India of differing colors (red, yellow, blue), with different amounts of iron (low, medium, high), and that used different filtration methods (no filter, sand filter). Table 6a-6c show the results of the calculated oxygen uptake based on the obtained data of endogenous and exogenous activities describing the oxygen uptake of R4H, R4M, R4L or R5H, R5M, R5L in the case of three dyes.

In the case of Reactive Red 120 dye, it was observed that for the samples with low iron surface area, oxygen uptake was found to be 0.00 nMol min⁻¹ mg⁻¹ for both R4L and R5L. This suggests that filtration had little effect on the sample, but partial oxidation for 40 minutes using an iron surface area of 161 cm² was not enough to leave the sample biodegradable for CETP sludge.

For the medium iron group, R4M had an oxygen uptake of 40.6 nMol min⁻¹ mg⁻¹ and 75.4 nMol min⁻¹ mg⁻¹ for R5M. Therefore oxidation for the same 40 minutes was enough for the partially oxidized sample to create biodegradability by CETP sludge, although almost double the

amount for the filtered sample. The group with high amount of iron was found to have zero theoretical biodegradability by CETP sludge for R5H and very low oxygen uptake of 3.84 nMol min⁻¹ mg⁻¹ for R4H.

Similarly, for Reactive Yellow 81 with low iron surface area, oxygen uptake was found to be 0.00 nMol min⁻¹ mg⁻¹ for R4L, and 101 nMol min⁻¹ mg⁻¹ for R5L. This suggests that filtration had a more substantial effect on the sample, and partial oxidation after 25 minutes using low surface area iron followed by sand filtration was enough to leave the sample biodegradable for CETP sludge. The medium iron group R4M had an oxygen uptake of 365 nMol min⁻¹ mg⁻¹ and 2.33 nMol min⁻¹ mg⁻¹ for R5M. Being partially oxidized for the same 25 minutes was enough for the sample to create biodegradability by CETP sludge, whereas the filtered sample had an extremely low oxygen uptake of 2.33 nMol min⁻¹ mg⁻¹, due to lack of nutrient availability for consumption. The group with a high amount of iron was found to have very low theoretical biodegradability by CETP sludge with or without filtration at 1.58 nMol min⁻¹ mg⁻¹ for R4H and 0.00 nMol min⁻¹ mg⁻¹ for R5H.

In the case of Reactive Blue 4 with low iron surface area, oxygen uptake was found to be 0.00 nMol min⁻¹ mg⁻¹ for R4L, and 0.00 nMol min⁻¹ mg⁻¹ for R5L. This suggests that filtration had little effect on the sample, but partial oxidation for 100 minutes using low surface area iron was not enough to leave the sample biodegradable for CETP sludge. For the medium iron group R4M had an oxygen uptake of 7.36 nMol min⁻¹ mg⁻¹ and 620 nMol min⁻¹ mg⁻¹ for R5M. Being oxidized for the same 100 minutes was enough for the partially oxidized sample to barely create biodegradability by CETP sludge, whereas the filtered sample had an extremely high oxygen uptake almost 100 times that of non-filtered. The group with high amount of iron was found to have no theoretical biodegradability by CETP sludge with or without filtration. Overall oxygen uptake results for reactive dyes show the greatest promise for biodegradability created after medium iron usage with or without filtration.

Results of three-way ANOVA used to statistically analyze the interaction between three different variables (color, iron surface area, filtration method) for the reactive dye experiments and how they affected respirometric analysis of the partially oxidized samples show that none of the three factors have a statistically significant effect on oxygen uptake (P>0.05). Also, the interaction effect was insignificant. It may be noted while the numbers of tests performed were too low to be statistically significant with regards to variables like iron surface area, the results do indicate that the process is beneficial, and there are indications that certain combinations are potentially better than others. For instance, medium iron tends to lead to oxygen uptake, indicating that pollutants are being consumed, while that is seen less with other iron surface areas.

In brief, it may be noted that the purpose of the studied photo-Fenton oxidation procedure was to completely degrade organic compounds from a reactive dye solution and to bring inorganics to the permissible drinking water level. The level of degradation achieved through various combinations of experimental variables described above and finally, the combined results obtained can be used to identify an experimental procedure that will achieve the most effective treatment of the dye effluent in a cost-effective and sustainable manner.

Since the work was not completed using laboratory-grade supplies, some contamination was expected to be found in the above results in the form of outliers in the analysis. Organic and inorganic chemicals found before (in the controls), during (after partial oxidation and followed by filtration), and after (after full oxidation, and followed by filtration) the

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sustainable photo-Fenton oxidation process, agreed with the previous literature studies [16,18,34-36]. The authors feel, since this study has a practical application because of the need for low-cost decolorization and dye wastewater treatment, it is necessary to prioritize the importance of certain variables over others in order to create a viable treatment unit to be used by small-scale silk dyers worldwide. The overall intention is to make sure that the color degrades and the chemical composition oxidizes to a simpler form before reusing the treated water for a second batch of dye, or before disposing of it as is normally done.

Conclusions

The following conclusions can be drawn from this study.

• This work has demonstrated that the photo-Fenton oxidation process is able to clean dye wastewater from cottage-scale textile industries using higher concentrations of dye in effluent that are not treatable by other means.

• There are many variables in the photo-Fenton oxidation process that impact the success of dye degradation. These include chemical composition of dyes, concentration of dye, acidified pH of solution, quantity of hydrogen peroxide used, solar irradiation, oxidation time, surface area of the scrap iron catalyst, and filtration method.

• Laboratory-scale studies using sustainable photo-Fenton oxidation to degrade 5 g/L dyes using pharmacy-grade 6% hydrogen peroxide, household hydrochloric acid, scrap iron sheets, and sunlight is best done for Reactive dyes using an intermediate amount of iron surface area (323 cm²) as the iron catalyst, while allowing for full oxidation time followed by sand and carbon filtration to remove sludge.

• The sustainable photo-Fenton oxidation process using scrap metal as the iron catalyst coupled with sand and carbon filtration shows great promise for the decolorization and chemical degradation of red, yellow, and blue colors in Reactive dyes. The process may not need biodegradation after complete oxidation and filtration, as little additional benefit was seen with biodegradation.

• The low-cost and simplicity of the sustainable photo-Fenton oxidation reactors may in the future offer a treatment option to cottage industries to implement this system quickly and easily in their own communities.

• Once the process grows past a pilot scale built for small-scale dye units, there is a great potential to scale up the system for larger units and commercial applications.

• Life cycle assessment (including O&M and labor costs) of low-cost photo-Fenton oxidation with filtration compared with biodegradation with reverse osmosis treatment is proposed for future work.

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