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DECOLOURIZATION OF DYE & TEXTILE EFFLUENT USING ADVANCED OXIDATION PROCESSES

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ABSTRACT

Increasing urbanization and industrialization have thus resulted in a dramatic increase in the volume of wastewater. The major industries contributing to water pollution are – textile mills, electroplating industry, metal processing industry, pulp and paper mill and tannery industry. Major pollution in textile effluent is due to high suspended solids, chemical oxygen demand, heat, color, acidity and other non-biodegradable substances. In order to tackle this menace of pollution problem, it is desirable to degrade the dye into non toxic form before its discharge into the main stream. Advanced Oxidation Processes are the one that offers a highly reactive, non-specific oxidant namely hydroxyl radicals ($HO^{\bullet}$), capable of destroying wide range of organic pollutants in water and wastewater. Fenton's reagent oxidation is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions. The main advantage of the Fenton's reagent is its simplicity in usage.

Keywords: Advanced Oxidation Process, Fenton & Photo Fenton Process, Hydroxyl radicals, Malachite Green Dye, Textile effluent.

I. INTRODUCTION

Industrialization is vital to nation's economy because it serve as a vehicle fordevelopment. Increasing urbanization and industrialization have thus resulted in a dramaticincrease in the volume of wastewater. Global water pollution scenario suggests thatnearly 1.5 billion people lack safe drinking water and at least 5 million deaths areattributed to waterborne diseases such as cholera, hepatitis every year. The majorindustries contributing to water pollution are textile mills, electroplating industry, metalprocessing industry, pulp and paper mill and tannery industry.

Major pollution in textile effluent is due to high suspended solids, chemicaloxygen demand, heat, color, acidity and other non-biodegradable substances. In order totackle this menace of pollution problem, it is desirable to degrade the dye into nontoxicform before its discharge into the main stream.

The traditional treatment techniques applied in textile wastewaters, such ascoagulation/flocculation, membrane separation (ultra-filtration, reverse osmosis) orelimination by activated carbon adsorption, only do a phase transfer of the pollutant, andbiological treatment is also not a complete solution to the problem. So AdvancedOxidation Processes (AOP´s), like Fenton and Photo-Fenton processes, could be a goodoption to treat and eliminate textile dyes. Advanced Oxidation Processes are theone thatoffers a highly reactive, non-specific oxidant namely hydroxyl radicals (HO•), capable ofdestroying wide range of organic pollutants in water and wastewater. Fenton's reagentoxidation is a homogeneous catalytic oxidation process using a mixture of hydrogenperoxide and ferrous ions. The main advantage of the Fenton's reagent is its simplicity inusage. In an acidic environment if hydrogen peroxide is added to an aqueous systemcontaining an organic substrate and ferrous ions, a complex redox reaction will occur.

1.1 Textile Wastewater

The textile industry in India guzzles double the accepted amount for consumption. A major factor is obsolete technology that permits minimum recycling and reuse of process water. For instance most textile mills in India do not use counter-washing systems instead they use clean water at every stage of the wash cycle. Discharges of highly colored dye effluents in natural water constitute one of the most important problems of the surface water [1]. The color is an evident indicator of water pollution by the dyes. Industrial dye effluents are visible even at concentrations lower than 1 mg/l. Synthetic organic dyes are generally recalcitrant in nature[2].

Composite textile wastewater is characterized mainly by measurements of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS) and dissolved solids (DS). Typical characteristics of textile industry wastewater are presented in Table 1.

Table 1: Composite Textile Industry Wastewater Characteristics [4]

Parameters	Values
pH	7.0 ─ 9.0
Biological Oxygen Demand (mg/L)	80 ─ 6000
Chemical Oxygen Demand (mg/L)	150 ─12000
Total Suspended Solids (mg/L)	15─ 8000
Total dissolved solids (mg/L)	2900 ─3100
Chloride (mg/L)	1000 ─1600
Color	50─2500

1.2 Fenton and Photo Fenton Processes

Fenton's reagent oxidation is a homogeneous catalytic oxidation process using amixture of hydrogen peroxide and ferrous ions. The main advantage of the Fenton'sreagent is its simplicity. The chemicals are readily available at moderate cost and there isno need for special equipment. In an acidic environment if hydrogen peroxide is added toa system containing an organic substrate and ferrous ions, a complex redox reaction willoccur [5].The overall reaction is:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{-} + HO^{\bullet} \qquad (1)$$

The ferrous ion initiates and catalyses the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals, $HO^{\bullet}$. Hydroxyl radicals are powerful oxidation agents that have an oxidation potential only lower than fluorine and higher than ozone and H_2O_2:3.0 V for fluorine, 2.8 V for $HO^{\bullet}$, 2.07 V for ozone and 1.78 V for

H_2O_2. Then, hydroxylradicals are capable of rapidly attacking organic substrates (RH) and cause chemicaldecomposition of these compounds by H- abstraction and addition to C─C unsaturatedbonds.

$$RH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O \quad (2)$$

$$R^{\bullet} + Fe^{3+} \rightarrow R^{+} + Fe^{2+} \quad (3)$$

$$R^{+} + H_2O \rightarrow ROH + H^{+} \quad (4)$$

Numerous competing reactions which involve Fe^{2+}, Fe^{3+}, H_2O_2, hydroxylradicals, hydroperoxyl radicals and radicals derived from the substrate, may also beinvolved. Hydroxyl radicals may be scavenged by reacting with Fe^{2+} or hydrogenperoxide:

$$HO^{\bullet} + Fe^{2+} \rightarrow HO^{-} + Fe^{3+} \quad (5)$$

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (6)$$

Fe^{3+} formed through reactions (1) and (5) can react with H_2O_2 following a radicalmechanism that involves hydroxyl and hydroperoxyl radicals, with regeneration of Fe^{2+}

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe - OOH^{2+} + H^{+} \quad (7)$$

$$Fe - OOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \quad (8)$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^{-} \quad (9)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^{+} + O_2 \quad (10)$$

In photo-Fenton process in addition to the above reactions the formation ofhydroxyl radical also occurs by the following reactions [1]. Theaddition of UV to Fenton's process could be an interesting option in dye decolourizationdue to its capacity to influence the direct formation of $OH^{\bullet}$radicals [4].

$$H_2O_2 + UV \rightarrow HO^{\bullet} + HO^{\bullet} \quad (11)$$

$$Fe^{3+} + H_2O + UV \rightarrow HO^{\bullet} + Fe^{2+} + H^{+} \quad (12)$$

II. MATERIALS & METHODS

2.1 Materials

2.1.1 Dye

In the present study Malachite Green, one of the most widely used basic dyes has been chosen as a model dye compound.Molecular structure &Physical and chemical properties of Malachite greenhas been illustrated in Table 2 & Table 3 respectively. Malachite green, also called analinegreen,basic green 4,diamond green B,orvictoria green B having IUPAC name 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N,N-dimethyl-aniline is a toxic chemical primarily used as a dye. It is a green crystalpowder with a metallic luster, very soluble in water, extremely soluble in ethanol,solutions are blue-green; basic green dyes become yellow in high concentration sulfuricacid, becomes dark orange when diluted; it becomes orange in high concentration nitricacid, becomes brownish orange when diluted.

Table 2: IUPAC Name, Molecular Structure, and Molecular Mass

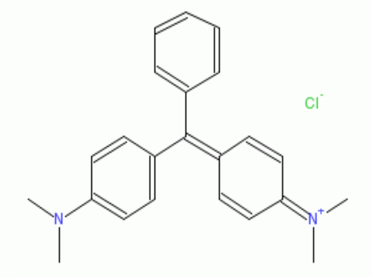
Name	IUPAC Name	Molecular Structure	Molecular Mass
Malachite green	4-[(4 dimethyl amino phenyl)-phenyl-methyl]-N, Ndimethyl-aniline		364.911 g/mol (chloride)

Table 3: Physical & Chemical Properties of Malachite Green

Physical State	Green Crystalline powder
Melting point	164^{o} C
Solubility in water	Soluble
Stability	Stable under ordinary condition
Odour	Less
Molecular weight	927.03
Polymerization	Will not occur
Toxic effect on human	Causes skin & severe Eye irritation
Charge	Positive electrical charge

2.1.2 Wastewater

Wastewater from the homogenous tank of effluent treatment plant(ETP,s) of textile industry is to be collected.

2.1.3 Chemical and reagents

Hydrogen Peroxide (H2O2) solution was purchased from S.D. fine-chemlimitedhaving 30% W/V AR and was freshly prepared. Hydrated ferrous sulfate (FeSO4.7H2O)was procured from SISCO Research laboratories, Mumbai, (extra pure AR) and was usedas such without purification. pH of the solutions was adjusted with 1M HCl or 1M NaOH.

2.2 Methods

2.2.1 Collection and storage of wastewater and dye sample

Collect sample from homogenous tank of effluent treatment plant of textileindustry. Sampling vessel are cleaned and rinsed carefully with distilledwater and then wash with sample during sample collection. Then effluent is stored incold store atatemp.of 4°C within 2 to 3 hrs of collection.Parameter to be studied includes pH, EC, TDS, BOD5, COD and turbidity.

2.2.2 Preparation of Solution

a) Dye Solutions: The dye solutions is prepared by adding a known amount ofdye into a small amount of deionized water in a 1-liter Erlenmeyer flask andfilling it to the mark with double distilled water. The flasks are covered withaluminum foil to avoid degradation by the laboratory fluorescent lights. Beforethe oxidation experiments could be performed, it is necessary to choose theappropriate concentration of dye solutions. For most of the experiments, dyesolutions of 25 ppm concentration is prepared by dissolving 0.025g indeionized water and make the solution quantity to1 L. (If 1 g is present in 1 L thensolution is said to be 1000 ppm and 0.1 g in 100 ml then it becomes 100 ppm)

b) Handling and Storage of Dye

Precautions:

Keep locked up. Keep away from heat. Keep away from sources ofignition. Empty containers pose a fire risk; evaporate the residue under a fumehood. Ground all equipment containing material. Do not ingest. Do not breathedust. Wear suitable protective clothing. In case of insufficient ventilation, wearsuitable respiratory equipment. If ingested, seek medical advice immediately andshow the container or the label. Avoid contact with skin and eyes. Keep awayfrom incompatibles such as oxidizing agents.

Storage: Keep container tightly closed. Keep container in a cool, wellventilatedarea. Do not store above 25°C (77°F).

c) Hydrogen Peroxide: Hydrogen peroxide (30% w/v) is obtained from S.D. finechem.Limited having M.W. of 34.01. It implies that 100 ml of solution contains30 g or 1 ml contains 300 mg. If this solution is diluted ten times then 1 mlcontains 30 mg of $H2O2$. Hence for adding 300 mg/l of $H2O2$ in dye or effluent,add 10 ml in 1 L of dye or 1 ml of diluted peroxide solution in 100 ml of dyesolution.

d) Ferrous Sulphate: Ferrous sulphate hydrated ($FeSO4.7H2O$) is prepared as10% w/v, which implies that the 10g of salt is dissolved in 100 ml of doubledistilled water. In order to dissolve ferrous sulphate completely in distilled water,few drops of concentrated sulphuric acid are added to shift the equilibrium ofreaction backward. Hence 1 ml of prepared solution contains 100 mg of salt. If thesolution is diluted ten times, then 1 ml contains 10 mg. For adding 150 mg/l, add15 ml in 1L of dye or 1.5 ml of diluted ferrous sulphate solution in 100 ml of dyesolution or effluent sample.

e) Calcium Hypochlorite: Sodium Hypochlorite (4 % w/v) is procured fromMerck, which implies 4 g of $NaClO$ is present in 100 ml of solution or 40 mg in1ml. For adding 40 mg/l of $NaClO$ in dye, add 1ml in 1 L or 0.1 ml in 100 ml.

III. CONCLUSION

- Fenton process has proved its superiority to other conventional methods of wastewater treatments, because of lack of toxicity of the reagents and due to simplicity of process.
- This technology leads to completely destruction of hazardous contaminants and avoid transfer of pollutants from one phase to another.
- In terms of commercial application, the main setback is the cost of reagents such as ozone, titania and hydrogen peroxide or energy light sources.
- A potential viable solution proposed is the combination of these processes with biological processing. In these combined processes, the chemical process would be utilized as pre-treatment step to enhance the biodegradability and eliminate the toxicity of the effluents, while the total mineralization would be completed in the conventional biological process.
- So it can be concluded that photo-oxidation system employing Fenton and solar light has potential to decolourize the textile dyes and is recommended as pretreatment step before conventional biological treatments for consideration at the WWTP.

- The future scope of this technology can be the replacement of H2O2 by any other suitable but less expensive oxidant. The by-products produced during treatments by UV, UV/H2O2/Fe2+, and H2O2/Fe2+ are unknown so more research is necessary to analyze the by-products in the effluent and their potential toxicity to stream organisms.

REFERENCES

[1]. Venceslau M.C., Tom S. and Simon J.J., (1994), “Characterization of textile wastewaters- a review”, Environmental Technology, **15**, 917-929.

[2]. Dae-Hee A., Won-Seok C. and Tai-Il Y., (1999),“Dyestuff wastewater treatment using chemical oxidation, physical adsorption and fixed bed bio film process”, Process Biochemistry, **34**, 429–439.

[3]. Adel Al-Kdasi, AzniIdris, KatayonSaed, ChuahTeong Guan (2005),” Treatment of textile wastewater by advanced oxidation processes-A review”, Global Nest, **6**, 222-230.

[4]. Marco S. Lucas,JoseA.Peres (2006),” Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation”, Science direct,**71**,236-244.