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TREATMENT OF TEXTILE EFFLUENT USING HETEROGENEOUS FENTON AND MICROFILTRATION

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ABSTRACT

In this study,the efficiency of combination of Heterogeneous Fenton (HF) and Microfiltration (MF) in treatment of textile waste water has been studied. Pretreatment has been conducted using Heterogeneous-Fenton using Fly ash. Pretreated textile waste water had chemical oxygen demand (COD) and Dye removal of 63.3% and dye removal 75% respectively. Successive trials were applied to evaluate the effects of parameters like pH, catalyst concentration (mg/L), H_2O_2 dosage (mM) and reaction time (min) on synthetic dye water treatment, in terms of COD and dye removal efficiencies. Post treatment of microfiltration with cellulose acetate has been conducted. The effect of parameters like pH, flow rate was studied. The result shows that, after combined treatment on optimum combination of parameters, at pH 3 and flow rate of 0.15 ml/sec the maximum removal of COD was 81.3%, and the maximum Dye removal was 89.6%.

***Keywords*: Cellulose Acetate, Heterogeneous -Fenton, Microfiltration**

I INTRODUCTION

The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes. Wastewater from printing and dyeing units is often rich in colour, containing residues of reactive dyes and chemicals, such as complex components, many aerosols, high colour, high COD and BOD concentration as well as much more hard degradation materials. The toxic effects of dye stuffs and other organic compounds, as well as acidic and alkaline contaminants from industrial establishments on the general public are widely accepted. At present, the dyes are mainly aromatic and heterocyclic compounds, with colour display groups and polar groups. The structure is more complicated and stable, resulting in greater difficulty to degrade the printing and dyeing wastewater [1]

Advanced oxidation processes (AOPs) especially the fenton process have been described as a promising option to remove persistent pollutants from contaminated water when conventional water treatment processes are not efficient enough. The heterogeneous Fenton processes with lower cost and friendly with the environment can overcome those disadvantages of the homogeneous Fenton processes [2]. In heterogeneous solid catalysts, the iron ions are 'immobilized' on the solid supports or within the structure and in the pore/interlayer of the catalysts. As a result, the catalysts can maintain its ability to generate hydroxyl radicals from hydrogen peroxide, and iron hydroxide precipitation is prevented. Besides showing limited leaching of iron ions, the catalysts can be

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easily recovered after the reaction, and remain active during successive basis of minerals or iron containing solid waste products such as kaolin, pyrite ash, fly ash and red mud. Fly ash is an industrial solid waste of burning power plants. Fly ash causes serious environmental pollution. Currently, fly ash can be used as additives or constructionmaterials, sorbents or catalysts forthe oxidation of H_2S, methane, sodium sulfite, decomposing dye [3].

Individual approach in reducing COD level shows high tolerance but the combination technique would give better performances. The precipitates formed after HF can be efficiently removed by a micro filter. Media like quartz, cellulose acetate, kaolin have been adopted as the major microfiltration membrane. Cellulose Acetate membranes offered a good combination of rejection, fouling resistance, and the ability to tolerate continuous chlorine up to 1.0 ppm [4].

The study thus investigates the potential of HF process and microfiltration as a combined treatment for removal of dye in textile waste water.

II METHODOLOGY

2.1 Sampling of real textile wastewater

Three samples of untreated real textile wastewater were collected at different intervals from Cannanore Handloom Exports. They were stored at 4°C and analysis was done for all the samples collected. The average values of the characteristics of untreated real textile wastewater are shown in the Table 1.

Table 1 Characteristics of untreated textile wastewater

Analytical Parameters	Value
COD (mg/l)	1050
BOD (mg/l)	380
pH	11
Turbidity (NTU)	41
Sulphide (mg/l)	30
Chloride (mg/l)	145
Hardness (mg/l)	130
Total Suspended Solids(mg/l)	48
Total Dissolved Solids (mg/l)	800

2.2 Preparation of Synthetic Wastewater

The synthetic wastewater was simulated towards the characteristics of a real textile dyeing effluent. Dyes were mixed in distilled water along with various chemicals like levelling agent, lubricant and wetting agent. The composition of the dye and various chemicals used in the synthetic sample preparation are given in the Table 2.

After the preparation of synthetic sample, the parameters like COD, Biochemical Oxygen Demand (BOD), turbidity, sulphide, chloride, hardness, alkalinity, Total Suspended Solids (TSS), and Total Dissolved Solids (TDS) were experimentally found out in the laboratory.

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2.3 Chemicals and Materials

The reactive dye Ramazol Turquoise blue was provided by Cannanore Handloom Exports textile industry in Kannur, and was used without further purification.Fly ash was collected from the Geotechnical Lab of GEC, Thrissur. Microfiltration cellulose acetate membrane of pore size 5 micron and surface area of 0.027 m^2 was purchased. All the chemical substances used in the experiment were of reagent grade. Sulphuric acid was used to adjust the initial solution pH.

Table 2 Composition of synthetic textile wastewater

Compound	Quantity
Ramazol Turquoise blue (Dye)	33 mg/l
Na_2CO_3	0.66 g/l
NaCl	0.7g/l
NaOH	0.63g/l
starch	1.44g/l
$Na_2S_2O_3$	0.34g/l
1N H_2SO_4	1 ml

2.4 HF Experiment

Catalyst was prepared supporting the metal by the incipient impregnation method. 6 g of $FeSO_4 \cdot 7H_2O$ dissolved in 20 mL of distilled water. After that, 10 g of fly ash added to the solution. The mixture stirred in water bath and heated at 100 ºC until the water completed evaporates. The sample dried at 100 ºC in an oven overnight. The catalyst samples obtained after heating at 500 ºC for 4 h [5].

The chemicals used in the experiment include 1N $H_2SO_4$to adjust the pH 30% H_2O_2 to generate peroxide radicals. 0.1N Sodium bisulphite ($NaHSO_3$) was added to stop the reaction of H_2O_2.

The HF experiment was carried out in a glass beaker of capacity 1L. The volume of the sample used was 250 mL. Then a given weight of prepared catalyst of fly ash and was added and mixed very well with wastewater for 10 min. and Given volume of H_2O_2 was added. The experimental setup was placed in orbital shaker. The reaction time starts with the addition of H_2O_2 and the reagents has to be thoroughly mixed. When required contact time is reached, 0.1N Sodium bisulphite ($NaHSO_3$) was added to stop the reaction of H_2O_2.

The factors influencing the Fenton reaction are pH, catalyst concentration and concentration of H_2O_2 and the reaction time. Several trials were done based on these factors. Range of variables is fixed based on previous study as shown in Table 3.

Table 3 Limits of Heterogeneous Fenton [5, 6]

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Parameter	Limits	
pH	2	5
Catalyst Concentration(g/L)	0.1	6
H_2O_2 Concentration (mM)	4	16
Reaction time (min)	30	180

2.5 MF Experiment

The setup mainly consists of two parts- a feed tank, a cross flow filtration unit. The overall process feed chamber capacity were 8L. The filtration unit was a spiral hollow wound membrane. The membrane module was kept within a container with an inlet and an outlet of capacity 1.8 L. The experiments were carried out at and 3 different pH. The pH process was adjusted to the required pH by adding dilute 0.1M H_2SO_4. Many of the systems of separation use pressure gradient as the main driving force, but here gravitational force was taken as the main driving force. And a head of 6 cm was kept in feed chamber throughout the study. These pretreated samples are passed through the container which contains the membrane and the outlet concentrations are measured at different stages using spectrophotometer. Permeate was collected every ten minutes and its COD and absorbance was measured. Filtration was carried out until dye concentration reached the constant limits. On completion of one set of analysis the used strip of cellulose acetate membrane was regenerated using sodium bicarbonate and trypsin solution.

III RESULTS AND DISCUSSION

3.1 HF Experiment

The factors influencing the Fenton reaction are pH, catalyst concentration and concentration of $H_2O_2$and the reaction time. Several trials were done based on these factors. The optimized condition of HF process using Fly ash is shown in Table 4.

If continue to increase the amount of catalyst, the performance not increase significantly but it even tended to decrease as shown in (1). The effectiveness of the treatment almost remained unchanged after 90 min of treatment at all levels of catalyst. It may be due to the self-scavenging of OH radical by converting it to hydroxyl ions during oxidation of Fe^{2+}.

$$Fe^{2+} + OH\cdot \rightarrow Fe^{3+} + OH^- \qquad (1)$$

Table 4Optimized condition of HF process

Parameter	Value
Catalyst Concentration	0.5

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(g/L)	
pH	3
H_2O_2 Concentration (mM)	11.02

This is consistent with the proved opinion that the optimum pH of Fenton oxidation mostly falls in the pH range of 2.5 to 3.5. In heterogeneous catalysis, the main source of OH□ radicals in Fenton type processes is the catalytic decomposition of H_2O_2. The low efficiency of applied heterogeneous process at pH 2 could be attributed to the stabilization of H_2O_2 that can form oxonium ion (H_3O^+) by solvating a proton asshown in (2). An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with ferrous ion.

$$H_2O_2 + H^+ \rightarrow H_3O^{2+} \qquad (2)$$

On the other hand, the reaction of hydrogen peroxide with Fe^{2+} is seriously affected due to the formation of complex species $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+,}$ which reacts slowly with hydrogen peroxide. In addition, the scavenging effect of the OH□ radicals is alsooccurring.

The decrease in performance of a large concentration of hydrogen peroxide can be explained by hydroxyl radicals partially consumed by the (3) [7,8].

$$H_2O_2{}^{+}\ HO\square \qquad HO\square_2 + H_2O \qquad (3)$$

Pretreatment has been conducted using HF using Fly ash at optimized condition. Pretreated textile waste water had COD and Dye removal of 63.3% and dye removal 75% respectively. The COD and BOD values reduced to 480 mg/L and 152 mg/L respectively. But these values not lie in the permissible limits of water standard.

3.2 MF Experiment

Separation experiment was performed using the filtration set up previously described using cross flow filtration technique. Feed solution was allowed to flow under gravity and whole module was perfectly sealed to avoid leakage. For the experiments, liquid feed was filtered at different pH and flow rate. Effluent of Heterogeneous Fenton using fly ash is adopted as the feed solution.

3.2.1 Effect of pH

pH is one of the strongest factors influencing the performance of the decomposition of organic matter in microfiltration techniques. Experimental results in 60 min collecting time and flow rate of 0.15 ml/sec are shown in Fig. 1 and Fig. 2. Experiment is conducted in pH 6, pH 7 and pH 8. The experimental results show that neutral environment is favourable for both dye and COD removal. The effect of the treatment tends to decrease in acidic and basic pH. The permeate flow was lowest at neutral pH compared to the rest, because the mechanism of flocculation of dye particles. This larger size flocculated dye particles cannot penetrate easily through the micro pores. So passage of dye particles gets blocked. But flocculation was less at acidic and basic solution. This will lead to the higher permeate flow rate and less rejection of dye particles [9].

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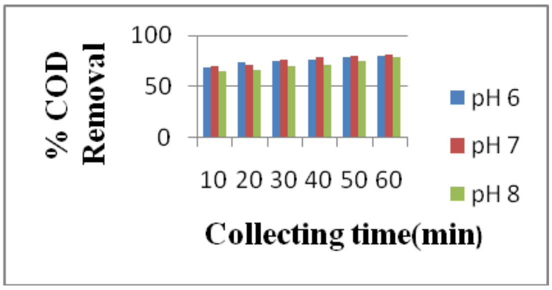

Fig. 1 Effect of pH on COD removal (at feed flow rate 0.15 ml/sec)

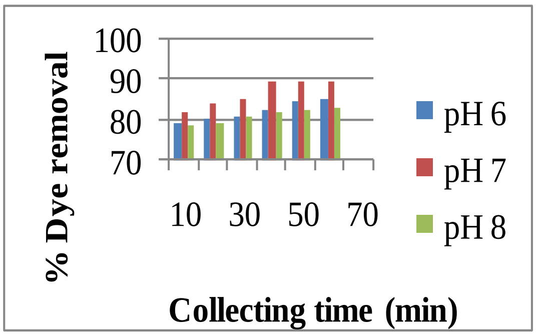

Fig. 2 Effect of pH on Dye removal (at feed flow rate 0.15 ml/sec)

3.2.2 Effect of Flow rate

Feed solution was allowed to flow under gravity. Experimental results in 60 min collecting time and at pH 7 are shown in Figure 3 and Figure 4. Experiment was conducted in different flow rate 0.15 ml/sec, 20 ml/sec, 55 ml/sec. Flow rate value selected on the basis of operating conditions of valve. The average percentage of rejection would be lower as the higher flow rate as stated in any membrane separation theory.

It was observed that the highest rejection percentage was at the feed flow rate of 0.15 ml/sec. It started with 81.8% and the rejection ended up at 89.6%. Overall, it was reasonable to conclude that the higher the flow rate, the higher would be the driving force which pushed the particles through the membrane pores. Thus, the formation of cake on the membrane surface would be minimized and lowered the percentage of rejection [9,10].

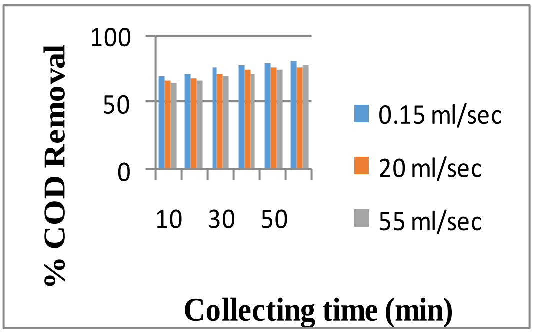

Fig. 3 Effect of flow rate on COD removal (at pH 7)

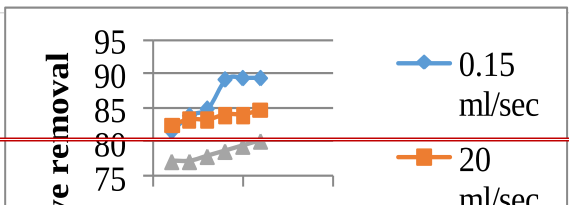

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Fig. 4 Effect of flow rate on Dye removal (at pH 7)

Thus microfiltration is optimized for COD and colour removal and the optimum parameters are obtained as 0.15 ml/sec influent flow rate and at pH 7. At pH 7, maximum dye removal was 89.6% and CODremoval was 81.3%. The pretreated wastewater was treated using microfiltration using cellulose acetate membrane at a pH 7and at a flow rate of 0.15 ml/ sec. Table 5 shows the characteristics of treated wastewater.

Table 5 Characteristics of treated wastewater

Parameter	After HF&MF
BOD (mg/L)	76
COD (mg/L)	244
pH	7.2
TSS (mg/L)	14.4
TDS (mg/L)	200
Chloride (mg/L)	30
Turbidity (NTU)	10
Hardness (mg/L)	32.5
Sulphide (mg/L)	3

IV CONCLUSIONS

Water pollution from textile dyeing industry becomes a matter of concern owing to significant organic matter and dyeing agents that produce colour and high amount of COD that is found to be toxic to biological life. A chemical treatment HF followed by a physical treatment of microfiltration can be used to treat textile wastewater effectively.

Initially, potential ability of fly ash as catalyst in HF process was determined. Reaction is optimized for COD and colour removal and the optimum parameters are obtained as 0.5 g/L catalyst concentration, 11.02mM H_2O_2 concentration, 90 min. reaction time and at pH 3. The COD and colour removal of 63.3% and 75% in the case of fly ash. Thus solar HF is an effective pretreatment for textile wastewater.

Microfiltration was done as a post treatment to HF to find out the efficiency of treatment of textile waste water. Microfiltration was carried at 3 pH and 3 flow rates. The filtration process shows maximum efficiency at pH 7, feed flow rate of 0.15ml/sec. At these conditions, 89.6% dye removal and 81.3% COD removal are obtained.

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COD removal of 78.3 % and 81.8 % dye removal was obtained with regenerated membrane Thus, Microfiltration with cellulose acetate membrane was found to be an effective post treatment method for dye removal. The treated wastewater can be discharged to into irrigation water since it meets the standards of Environmental protection act 1986.

REFERENCES

[1] Kim H. T., Lee Y., Yang J., Lee B. and Park C. H., 'Decolourization of dye solution by a membrane bioreactor using whiterot fungi', *Desalination,Vol. 168*, 2004, pp. 287-293.

[2] Papadopoulos A. E., Fatta D. and Loizidou M., 'Development and optimization of dark Fenton oxidation for the treatment of textile wastewaters with high organic load', *Water Resources, Vol. 36*, 2007, pp. 558-563.

[3] Duc D. S., 'Degradation of Reactive Blue 181 Dye by Heterogeneous Fenton Technique Using Modified Fly Ash', *Asian Journal of Chemistry, 25(7),*2013, pp. 4083-4086.

[4] Sathiyamoorthy M., Gashaw M., Tesfaye M., Yilma M.,Tasew T. and Fantahun N., 'The removal of colour from synthetic textile dye effluent using Cellulose acetate reverse osmosis membrane', *International Journal of Advanced Research in IT and Engineering, Vol.1*,2012, pp. 25-42.

[5] Flores Y., Flores R. and Gallegos A. A., 'Electrostatic precipitation', *Journal of Molecular Catalysis, Vol.28*, 2008, pp.184- 191.

[6] Hassan H. and Hameed B. H., 'Fe–clay as effective heterogeneous Fenton catalyst for the decolorization of Reactive Blue 4', *Chemical Engineering Journal, Vol.171,*2011, pp. 912-918.

[7] Rahmani A. R., Zarrabi M., Samarghandi M. R., Afkhami A. and Ghaffari H. R., 'Degradation of Azo Dye Reactive Black 5 and Acid Orange 7 by Fenton-Like Mechanism', *Iranian Journal of Chemical Engineering. Vol. 7*, 2010, pp. 87-94

[8] Sanchez P. T., Marcos J., Rios S., Hernandez I. L. and Miranda V. M., 'Adsorption-regeneration by heterogeneous Fenton process using modified carbon and clay materials for removal of indigo blue', *Environmental Technology,Vol.4*, 2015, pp. 1-43.

[9] .Ahamad A. L., Haris W. A., Syafiie and Seng O. B., 'Removal of dye from wastewater of textile industry using membrane technology', *Journal of technology, Vol. 36,* 2002, pp. 31-44.

[10] 7. Giwa A. and Ogunribido A., 'The Applications of Membrane Operations in the Textile Industry: A Review', *British Journal of Applied Science & Technology, Vol. 2(3),*2012, pp.296-310.