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UV Assisted Fenton Oxidation of Organics Present in the Reverse Osmosis Concentrate of a Textile Waste Water Treatment Plant

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Abstract **- The concept of zero discharge is accelerated in the mean time on the rising trend of discharging the waste water by the industries which have been identified under red category by the Ministry of Environment and Forest, Government of India. Textile dyeing is one such industry where the implementation of zero discharge from the textile water treatment plant. In practical cases there are plethoras of difficulties because the concentrate of reverse osmosis is coloured, highly alkaline and high COD content. This paper deals about the attempts of removal of color and COD from the reverse osmosis concentrate. In this paper the reverse osmosis concentrate is been subjected to UV radiations with homogenous catalyst like Ferrous, Copper ions and Manganese ions. The results of the concentrate in COD content varied in the duration of 2hours with the usage of catalyst. However, it is found that COD reduction is highest in the combined catalyst of ferrous and copper ions. Further color removal was also observed. This treated effluent is further treated with nano filtrations, reverse osmosis or evaporator to achieve zero discharge.**

Keywords - Fenton Oxidation, Zero discharge, Reverse Osmosis Concentrate

I. INTRODUCTIONs

Textile is one of the oldest industries in the world with a major contribution to the economy of the nation. In India the contribution from the textile industries amounts to approximately 5% and 27% to the foreign exchange earnings. Specifically in TamilNadu the regions around Coimbatore, Tirupur, Karur, Erode is referred as "Textile Valley of India". Tirupur generates an export around Rs 50,000 million per year and Karur Rs 35,000 million per year in foreign exchange from textile industries.

Large amount of water is been consumed by the industries for the dyeing process and for the production of different types of fabrics. The water discharged from the industries has large amount of hazardous chemicals and dyes in it which affects the environment. The textile effluent is characterized by colour, pH, BOD/COD ratio, Total Dissolved Solids (TDS), Suspended solids. The textile reject treatment is a complicated problem due to the following reasons

- High Total Dissolved Solids (TDS) content
- Presence of Heavy chemical such as Cr, As, Cu, Zn
- Non Biodegradable organic dye stuffs
- Presence of free chlorine and dissolved silica

In the textile reject there are large amounts of undigested organics. Inorder to oxidize the organic particles present in wastewater it is essential to use oxidation process. The organic particles present in the textile reject is digested in the presence of more heat energy so as to induce high amount of heat energy for the digestion of organic particles makes a necessity towards Advanced oxidation process(AOP) as the conventional treatment process was unable to degrade the coloured dyes and toxicity. There are four ways for Advanced Oxidation Process

- Combination of Ozone (O_3)/ Hydrogen Peroxide (H_2O_2)
- Combination of Ozone (O_3)/ Ultra Violet Radiations
- Combination of Ultra Violet (UV) Radiation Hydrogen Peroxide (H_2O_2)
- Combination of Ozone (O_3)/Ultra Violet Radiation/ Hydrogen Peroxide (H_2O_2)

This paper deals with Advanced Oxidation Process by the combination of Ultraviolet radiations (UV) and hydrogen peroxide (H_2O_2) for the degradation of COD in the textile reject. On the exposure of Ultra violet radiations, hydrogen peroxide will be photolyzed to form hydroxyl radicals as the primary oxidant. This hydroxyl radical digests the organic molecules and thereby reducing the chemical contamination and toxicity in the textile reject.

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In order to make a complete ecofriendly atmosphere led to the concept of zero discharge. This is considered to be beneficial to the textile industries and to the environment. This is a most advanced waste water treatment plant which reuses the waste water in such a way that water is free from impurities and chemicals. The main aim of the zero discharge is to recover the usable materials like water, salt from the effluent and minimize the generation of waste so that it can be safely stored on site without the need for discharge into the environment.

II. OBJECTIVES

The main objective of the project is to reduce the COD content in the textile reject using Advanced Oxidation Process. The reduction of COD content in textile reject is being carried out by the exposure of Ultraviolet rays with different types of Catalyst like Ferrous (Fe^{2+}), Copper ions (Cu^{2+}) and Manganese ions (Mn^{2+}).

III. MATERIALS AND METHODS

SAMPLE COLLECTION

The textile reject is collected from the textile waste water treatment plant in SIPCOT, Perundhurai, TamilNadu, India. The collected textile reject consists of large amount of Suspended Solids, BOD and COD. The reject is the effluent collected after primary (aeration) and secondary (reverse osmosis) treatment. The textile effluent characteristics like pH, Total Dissolved Solids (TDS), COD and Chloride were determined in the collected raw textile waste water given in the table 1

Table 1: Characteristics of Textile Effluent collected from reverse osmosis concentrate stream

pH	7.75
TDS (mg/l)	23,000
COD (mg/l)	790
Conductivity (µ Siemens)	35,300
Chloride (mg/l)	78,500

CATALYST USED

- Ferrous ions (Fe^{2+})
- Copper ions (Cu^{2+})
- Manganese ions (Mn^{2+})
- Combination of Ferrous ions (Fe^{2+}) and Copper(Cu^{2+})
- Combination of Ferrous ions (Fe^{2+}) and Manganese ions (Mn^{2+})

KINETICS UNDER UV LIGHT

The setup of the sample is shown in figure 1 and it consists of beaker with a nozzle, Quartz Test Tube, UV light (primary radiation at 254nm)

Figure 1: UV Photoreactor

Before performing the kinetics in the apparatus, the procedure is followed initially the beaker is filled with 100ml of the collected sample and the catalyst with hydrogen peroxide (1:1 of 5ml) is added in the sample and stirred thoroughly without any air bubbles in the beaker. Before starting the process collect a 3ml sample by the use of syringe which is considered as a sample for zero minutes. After the start of the process for every 15minutes a sample of 3ml is taken continuously up to 2 hours. This procedure is repeated using different types of catalyst. The collected samples are placed in the COD photometer for the determination of COD content.

COD PHOTOMETER

2ml of the sample is taken in the COD vial with the reagent present in it. The vial is made to mix thoroughly with the reagent and placed in the digestor for a period of 2hours. After 2 hours the vial is allowed to cool and it is placed in the COD photometer for the determination of COD content.

IV. RESULTS AND DISCUSSIONS

REACTION KINETICS OF TEXTILE REJECT WITH FERROUS (Fe^{2+}) AS CATALYST

The readings shown below are obtained with Ferrous (Fe^{2+}) as catalyst, hydrogen peroxide as oxidant. The COD: Hydrogen peroxide (H_2O_2): Catalyst mixed in the molar ratio of 1:1:1. This mixture is exposed to Ultra violet (UV) radiations for 2hours. Samples were taken out in the interval of 15minutes for 2 hours and COD is measured. The results are tabulated in the table 2. Inorder to find the rate constant, the ratio between initial concentration of COD (A_0) and the

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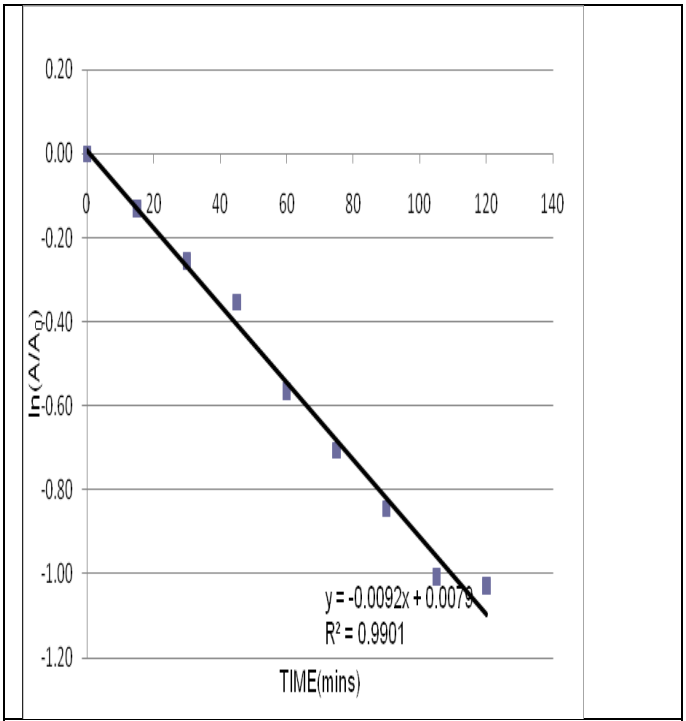
concentration of 15mins interval (A) is plotted against time in the Graph 1. The COD reduction from the table 2 is 64% in 2hours. The calculated rate constant for this type of catalyst is -0.0092.

Table 2: Kinetics of UV- Fenton Oxidation of Organics present in the textile effluent with Ferrous (Fe^{2+})as catalyst
The COD: Hydrogen peroxide (H_2O_2): Catalyst (Fe^{2+})mixed in the molar ratio of 1:1:1

Time (min)	COD (mg/l)	A_0 / A	ln(A_0 / A)
0	389	0	0
15	341	0.877	-0.131
30	301	0.774	-0.256
45	273	0.702	-0.340
60	221	0.568	-0.556
75	192	0.494	-0.705
90	167	0.429	-0.846
105	142	0.365	-1.008
120	139	0.357	-1.030



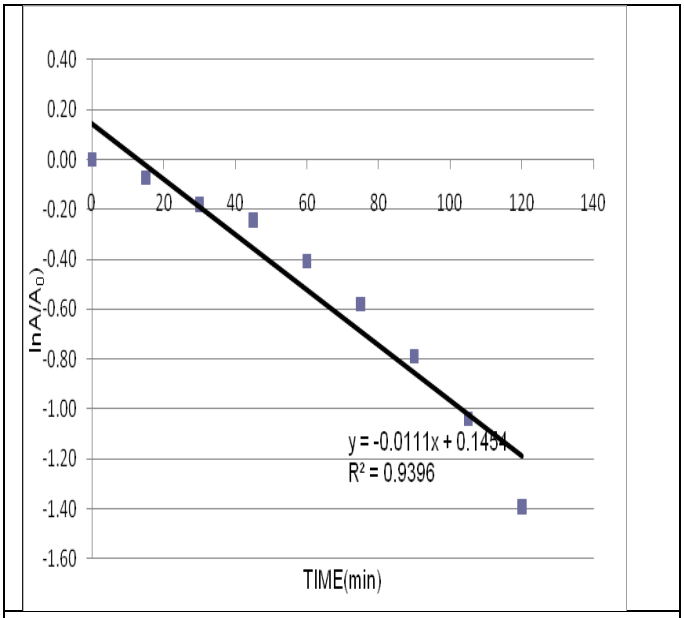
Graph 1: Kinetics of UV Fenton Oxidation of organics present in the textile effluent using Ferrous (Fe^{2+})as catalyst

REACTION KINETICS OF TEXTILE REJECT WITH COPPER IONS (Cu^{2+}) AS CATALYST

The sample is mixed with Copper ions (Cu^{2+}) as catalyst and hydrogen peroxide as oxidant is subjected to Ultra violet radiations (UV). The readings are tabulated in Table 3 and the respective graph in Graph 2 is plotted for the determination of rate constant. The COD reduction using copper ions is calculated as 42% with rate constant of -0.00344.

Table 3: Kinetics of UV- Fenton Oxidation of Organics present in the textile effluent with Copper ions (Cu^{2+})as catalyst
The COD: Hydrogen peroxide (H_2O_2): Catalyst (Cu^{2+}) mixed in the molar ratio of 1:1:1

Time (min)	COD (mg/l)	A_0 / A	ln(A_0 / A)
0	381	0	0
15	293	0.769	-0.283
30	284	0.745	-0.314
45	280	0.734	-0.328
60	271	0.711	-0.361
75	224	0.589	-0.551
90	244	0.640	-0.466
105	263	0.690	-0.391
120	222	0.582	-0.561



Graph 2: Kinetics of UV Fenton Oxidation of organics present in the textile effluent using Copper ions (Cu^{2+})as catalyst

REACTION KINETICS OF TEXTILE REJECT WITH FERROUS ($Fe2^{+}$) AND COPPER IONS (Cu^{2+}) AS A CATALYST

The COD reduction is a combination of Ferrous (Fe^{2+}) and Copper ions (Cu^{2+}) as a catalyst with equimolar concentration with (1:1) ratio. The COD reduction is calculated from the table 4 as 81.15% and the corresponding rate constant is determined from the Graph 3 as -0.01441. This combination of catalyst shows the higher amount of COD reduction compared to other conditions that is organic particles in the reject is broken in higher rate.

Table 4: Kinetics of UV- Fenton Oxidation of Organics present in the textile effluent with Ferrous (Fe^{2+}) and Copper ions (Cu^{2+})as catalyst
The COD: Hydrogen peroxide (H_2O_2):: Catalyst (Fe^{2+}) and (Cu^{2+}) mixed in the molar ratio of 1:1:1

Time (min)	COD (mg/l)	A_0 / A	ln(A_0 / A)
0	389	0	0
15	341	0.876	-0.132
30	304	0.781	-0.247
45	283	0.727	-0.318
60	222	0.570	-0.562
75	167	0.429	-0.846
90	124	0.318	-1.145
105	93	0.239	-1.431
120	72	0.185	-1.687

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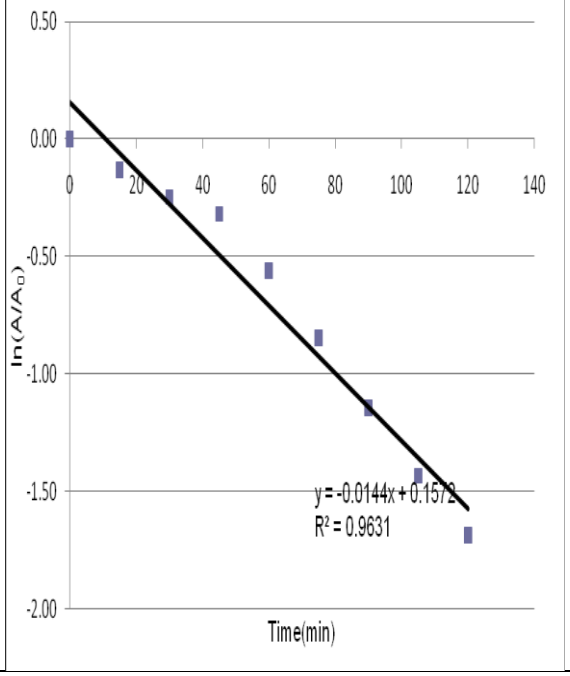
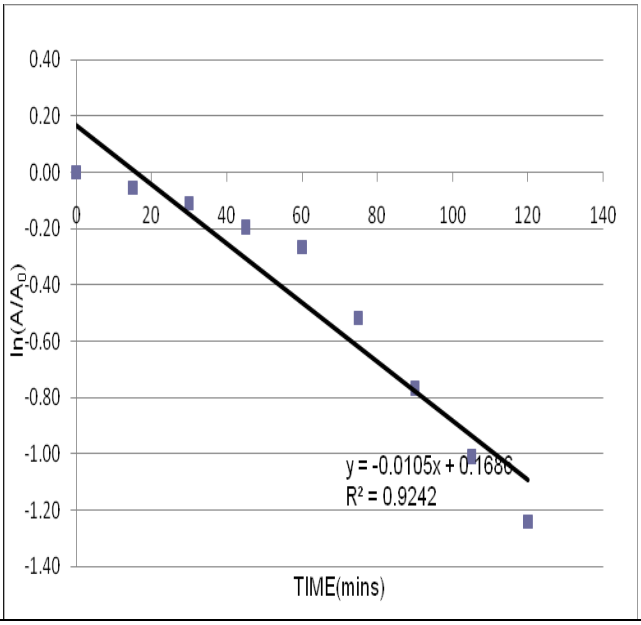


Graph 3: Kinetics of UV Fenton Oxidation of organics present in the textile effluent using Ferrous (Fe^{2+}) and Copper ions (Cu^{2+})as catalyst

REACTION KINETICS OF TEXTILE REJECT WITH FERROUS (Fe^{2+}) AND MANGANESE IONS (Mn^{2+}) AS A CATALYST

The results of COD are shown in table 5 and the rate constant is calculated from the Graph 4. Thus the COD reaction in method is found to be 71.15% and the rate constant is 0.01054



Graph 4: Kinetics of UV Fenton Oxidation of organics present in the textile effluent using Ferrous (Fe^{2+}) and Manganese ions (Mn^{2+}) as catalyst

COMPARISON OF THE OBTAINED RESULTS

Table 6: Summary of Experimental Results

Experiment No	Catalyst	Rate Constant	R^2	COD Reduction after 2hours (%)
1	Ferrous(Fe^{2+})	0.009	0.990	64.10
2	Copper ions (Cu^{2+})	0.003	0.702	41.70
3	Combined Ferrous(Fe^{2+}) and Copper ions (Cu^{2+})	0.014	0.963	81.49
4	Combined Ferrous(Fe^{2+}) and Manganese ions (Mn^{2+})	0.011	0.924	71.15

V. CONCLUSIONS

The importance of the usage of advanced oxidation process for the treatment of textile waste water is emphasized because higher level of TDS content in the textile reject makes unsuitable for biological treatment process. This paper focus on the attempts to remove the color and COD in the textile reject using various homogenous catalyst like Ferrous (Fe^{2+}), Copper ions (Cu^{2+}), Combined Ferrous (Fe^{2+}) and Copper ions (Cu^{2+}) and Combined Ferrous(Fe^{2+}) and Manganese ions (Mn^{2+}) employed here. A maximum of COD reduction 81.49 % is achieved in Combined Ferrous (Fe^{2+}) and Copper ions (Cu^{2+}) and the least amount of COD reduction 41.70% in Copper ions (Cu^{2+}) catalyst. Further color removal was also observed. Hence this process can be adopted by the textile industries for achieving zero discharge.

Table 5: Kinetics of UV- Fenton Oxidation of Organics present in the textile effluent with Ferrous (Fe^{2+}) and Manganese ions (Mn^{2+}) as catalyst

The COD: Hydrogen peroxide(H_2O_2):: Catalyst (Fe^{2+}) and (Mn^{2+}) mixed in the molar ratio of 1:1:1

Time (min)	COD (mg/l)	A_0 / A	ln(A_0 / A)
0	371	0	0
15	351	0.946	-0.055
30	332	0.894	-0.112
45	305	0.822	-0.196
60	284	0.765	-0.267
75	221	0.595	-0.519
90	172	0.463	-0.770
105	135	0.363	-1.013
120	107	0.288	-1.244

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