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Treatment Of Textile Dyeing Wastewater By Modified UV Photo-Fenton Process Using A New Composite Steel Scrap /H₂O₂

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Abstract--This paper evaluates the treatment of textile dyeing wastewater using new composites as adsorbents and / or heterogeneous catalysts for Modified UV-Fenton oxidation. The efficiency of the process was explored as a function of the experimental parameters: pH, hydrogen peroxide concentration and Steel scrap catalyst content. The composites with high Steel scrap content were effective to adsorb colour and COD in textile dyeing wastewater, and the adsorptive capacity increased with the superficial iron concentration. These Steel scrap was also used as heterogeneous catalyst and had the advantage of being effective at pH 3.0 with a consumption of H₂O₂ lower than required by the homogeneous Fenton process.

Keywords--Advanced oxidation technologies, Heterogeneous catalyst, Textile dyeing wastewater.

I. INTRODUCTION

The textile industry produces large volumes of effluents that contain appreciable quantities of organic compounds which are not easily amenable to chemical or biological treatment. The non biodegradability of textile wastewater is due to a high content of dyestuffs, surfactants and additives which generally are organic compounds of complex structures. These compounds can be removed by adsorption onto porous solids, but this process only transfers the contaminant from the liquid phase to the solid phase. Advanced oxidation processes show potential as one of the technologies for treating refractory compounds in textile wastewaters.

The combination of hydrogen peroxide and a ferrous salt has been referred to as Fenton reagent [1, 2, 3]. Heterogeneous oxidation involves intensive contacting of an organic compound in solution with oxygen over a solid catalyst.

Although the use of the catalyst makes the reaction conditions milder than uncatalyzed wet oxidation, the catalytic process still requires moderate temperature and pressure [4, 5].

Iron oxides are effective catalysts for catalytic wet hydrogen peroxide oxidation [6,7, 8, 9] and this process is also called heterogeneous Fenton degradation. These heterogeneous processes are promising because homogeneous processes need a separation step of iron sludge at the end of the reaction. However only a few attempts have been made to evaluate the potential of heterogeneous Fenton process.

The activity of the catalyst depends on characteristics of the iron oxides, such as crystallinity [8,10,11] and surface area [12]. However, it has been demonstrated that iron oxide catalysts lose their activity because of leaching effects of metallic catalysts in acidic medium [12,13]. Effects of heterogeneous catalysts for Fenton oxidation are also suitable for adsorptive filtration [1,14].

In this work, we studied the treatment of textile dyeing wastewater by adsorption and simultaneous catalytic wet hydrogen peroxide oxidation using new composite Steel Scrap/H₂O₂ and evaluated the effects of the pH, H₂O₂ concentration and catalyst dosage on the efficiency of the treatment.

II. EXPERIMENTAL

2.1 Material

The Steel scrap used as an adsorbent / catalyst. The adsorbent steel scrap was characterized through the determination of their specific BET area and iron content. This Steel scrap has presented high capacity for removal of iron dissolved in water (15, 16).



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The morphologic analysis and mapping of the elementary composition of Steel scrap was determined by scanning electronic microscopy (SEM / EDAX).

Characterization of textile dyeing wastewater

The textile wastewater was obtained from a textile industry at Tirupur, Tamilnadu, India, during April month. Samples taken were preserved in the refrigerator at 4°C in accordance with the Standard methods for the Examination of Water and Wastewater (APHA.,2002). The characteristics of raw effluent are listed in Table 2.

Table 1.
Characteristics of the raw textile dyeing effluent

Sl.No	Characteristics	Value
1	Colour,Absorbance in nm	0.433
2	COD, mg/L	1840
3	pH	8.41
4	Chlorides, mg/L	476
5	BOD ₃ , mg/L	695

2.2. Methods

The capacity of adsorption of the Steel scrap was determined experimentally by contacting the wastewater with different dosages of scrap in the range 10 g / L to 60 g/L at different initial pH. The adsorption and simultaneous heterogeneous photo Fenton oxidation were carried out using different dosages of Steel scraps, in the range 10g/L to 60g/L and hydrogen peroxide concentration in the range of 10 mL/L-15 mL/L, at different initial pHs. In a typical run, 250ml of textile wastewater was added to the reactor together with the Steel scrap. The mixture was agitated during 15min at 90rpm and the pH was adjusted to the desired value using 1N H₂SO₄. Then, H₂O₂ added to achieve the desired H₂O₂ concentration and the mixture was agitated at 90 rpm during 120 min.

After treatment, the samples were centrifuged at 3000rpm in 5min and the liquid was analyzed in order to determine the residual hydrogen per oxide concentration, COD and colour.

III. RESULTS AND DISCUSSION

3.1. Chemical and textural characterization of Steel scrap

The textural characteristics of steel scrap are summarized in table.2.The solids presents a small surface area with a wide pore sizes distribution.

Table2.
Characterization of the steel scrap

	Steel scrap
BET surface area (m ² /g)	0.5192
Micropore volume (cm ³ /g)	1.8 x 10 ⁻³
Micropore width (nm)	3.1
Pore size distribution(%)	
Micro	49.8
Meso	14.5
Macro	25
Point of zero charge	6.5-7.5

3.2. Chemical Composition and Morphologic Analysis of Steel Scrap

The steel scrap is produced during metal sawing was washed and dried at 103°C. The heated Steel scrap was cooled and separated by a sieve to get uniform size. The particle size of steel scrap used in the study was in the range of 0.5-2 mm. The chemical composition of the Steel scrap used as a catalyst is shown in Table 3. The morphologic analysis of steel scrap used as a catalyst is shown in Fig.1. The solids present an irregular surface and the small particle aggregates are observed.



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Table 3.
Chemical composition of the scrap used as a catalyst in percentage by weight

C	O	Fe	Si	Mn	Ca	Mo	Al	Trace Elements
41.39	8.77	45.91	1.20	0.46	0.50	0.35	0.31	1.11

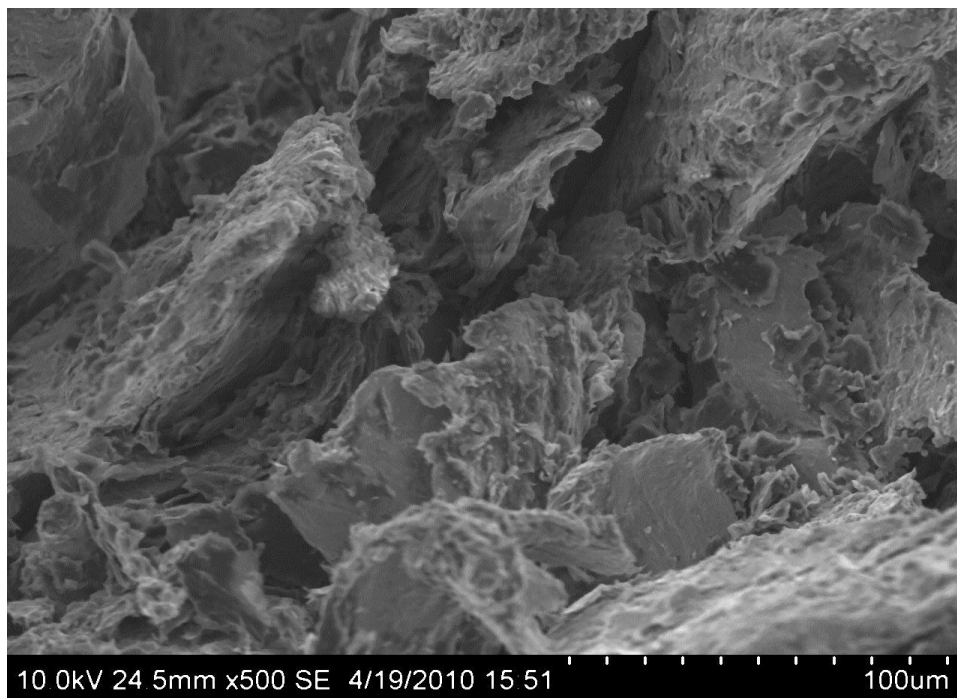


Fig 1: Morphologic analysis of Steel scrap used as catalyst

3.2. Textile wastewater adsorption on to Steel scrap catalyst

The contact of the effluent with the solids for 5h at 27°C, pH 8.41 and different dosage of solids showed that the

colour and COD removal of 96% and 69% respectively as shown in Fig 2.



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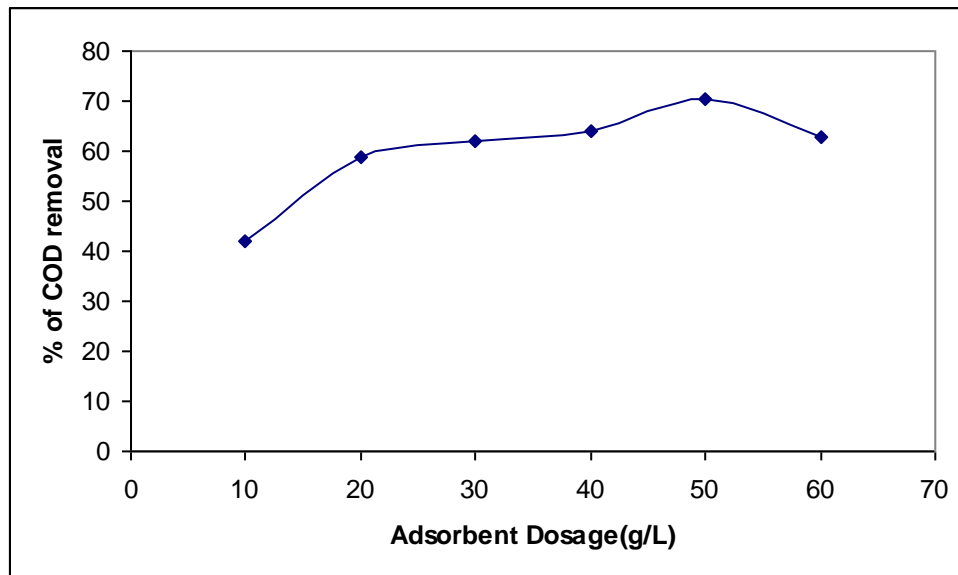


Fig 2. Effect of catalysts dosage on COD removal (Contact time 5 h, pH 8.41, t = 27°C)

The adsorptive capacity of the Steel scrap catalyst depends on the iron oxide content. Iron oxides aggregates have special characteristics in aqueous solution and are present as ferrihydrite in a gelatinous and insoluble coverage on the adsorbent carbon surface with adsorptive capacity.

3.4. Degradation of textile wastewater by Modified Fenton oxidation:

The concentration of iron in the liquid phase was measured during the reactions and the results showed that negligible amount of iron oxides was leached to the liquid phase then; no contribution of the homogenous Fenton reaction during the degradation of textile wastewater by heterogeneous Fenton oxidation could be expected.

The kinetics of COD removal by Modified Fenton oxidation was studied using 50g / L of scrap catalyst at initial pH3 (Fig3). The kinetics can be divided in two steps: a fast first stage followed by a slow stage. This behavior was also observed in the homogeneous Fenton and can be explained considering that hydrogen per oxide reacts quickly with iron oxide on the solid's surface to produce a great quantity of hydroxyl radicals. The hydroxyl radicals produced can react rapidly with the organic matter. The oxidation iron on the solid's surface produced in the first stage could react with hydrogen per oxide to produce hydroperoxyl radicals and regenerating the catalyst the solid's surface. As the hydroperoxyl radical is less oxidative than the hydroxyl radicals (3), a slow second stage occurs.



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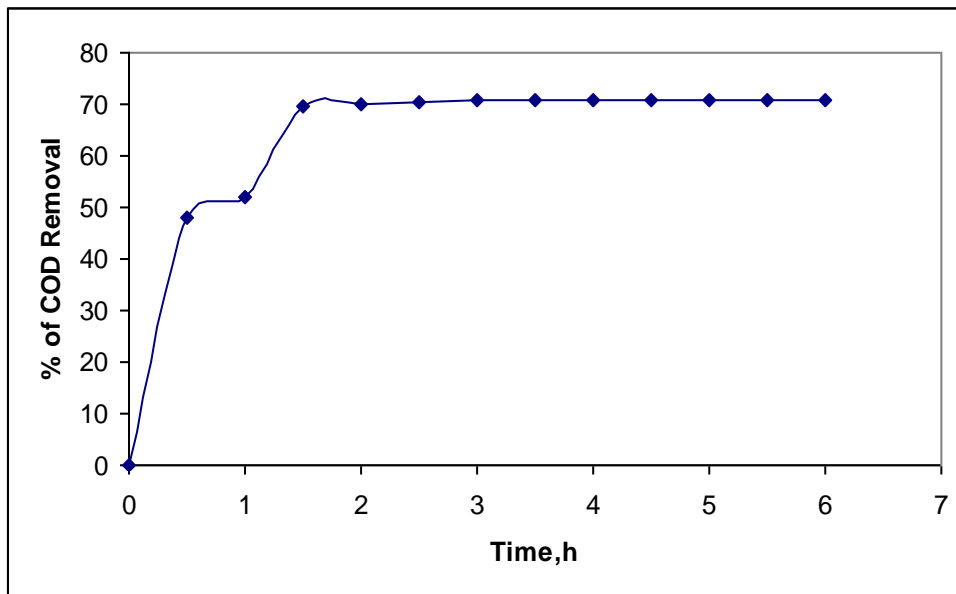
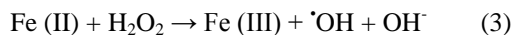
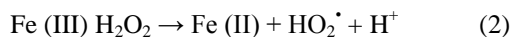
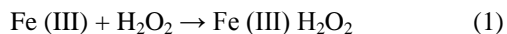


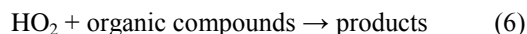
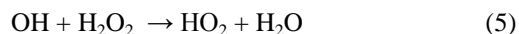
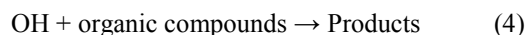
Fig 3 Kinetics of COD Removal by heterogeneous Fenton reaction using steel scrap as a catalyst(steel scrap dosage 50 g/L, H₂O₂ = 15 mL/L,pH = 3,T=27°C)

The kinetics of hydrogen peroxide disappearance was also evaluated during the wastewater degradation. The mechanism of H₂O₂ decomposition on iron oxides and hydroxides was recently reported by Kwan (9), and can be described according to Equations (1) – (3). The controlling step would be the surface reaction between hydrogen peroxide adsorbed on the solid's surfaces and the iron oxides. Then, the rate of formation of hydroxyl radicals (OH) depends on the iron oxide content.



The site (Fe III) represented in Equation (1) is regenerated through Equation (3) and it has been suggested that the adsorption of Hydrogen per oxide (Equation 1) is much faster than that of the others (9).

The hydroxyl radicals (OH) formed in Equation could oxidize organic compounds presents in the textile wastewater (Equation 4) or react with hydrogen per oxide in the liquid phase to form hydroperoxyl radicals (Equation 5) (3) that react slowly with organic compounds (Equation 6)



The COD removal is maximum at the catalyst dosage of 50g/L (Fig.4)



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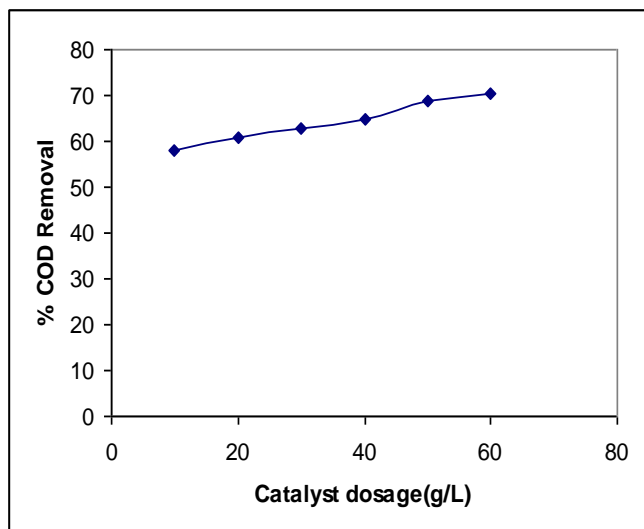


Fig 4. Effect of catalyst dosage on COD removal by heterogeneous Fenton Oxidation ($H_2O_2 = 15 \text{ ml/L}$, $pH = 3$, Reaction time = 1h, $T=27^\circ\text{C}$)

The removal of colour and COD by adsorption decreases as the pH increases but the heterogeneous Fenton reaction is much less sensitive to pH than the homogeneous Fenton reaction (20). Some authors have reported that the catalytic wet hydrogen peroxide oxidation depends on the pH when the reaching of iron varies with the pH (1, 7).

3.5. Effect of hydrogen peroxide concentration on the degradation of textile wastewater by heterogeneous Fenton reaction.

It was previously reported (15) that the enhancement in the hydrogen peroxide concentration from 10ml/L to 20 ml/L increases the COD removal by homogeneous Fenton oxidation from 58 to 69%. However, no increase in the COD removal by heterogeneous Fenton oxidation using steel scrap was observed, and low H_2O_2 concentration was necessary to achieve 71% of COD removal using scrap.

As shown in Equation (1) – (4), the heterogeneous oxidation of the organic matter occurs after the adsorption and decomposition of hydrogen peroxide on the solid's surface. The reaction represented in Equation (1) is fast and reaches pseudo equilibrium according to the Langmuir model.

The maximum COD removal achieved in the treatment of the same textile wastewater by homogeneous Fenton oxidation is nearly 70 % using H_2O_2 concentration of 15 ml/L at pH 3.0.

The heterogeneous Fenton oxidation using scrap as catalyst achieved 73 % COD removal at room temperature using H_2O_2 concentration lower than 15 ml/L, and presented the additional advantage of being less sensitive to pH than the homogeneous process.

IV. CONCLUSION

Composites of Steel scrap/ H_2O_2 can be used in the treatment of textile wastewater heterogeneous catalyst in the UV Fenton reaction. The adsorptive capacity of these solids increases as the superficial iron oxide content increases. The treatment of textile wastewater using these heterogeneous catalysts can be carried out at initial pH above 3 and lower hydrogen peroxide consumption than in the homogeneous Fenton process is needed. No iron was reached to the aqueous Fenton reaction was not important and the catalyst in quite stable.

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