

Adsorption Characteristics of Steel Scrap used as Heterogeneous Catalyst in Fenton Process in Textile Dyeing Wastewater Treatment

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ABSTRACT

This paper evaluates the treatment of textile dyeing wastewater by using steel scrap as adsorbents and heterogeneous catalysts for Modified Fenton oxidation. The efficiency of the process was explored as a function of the experimental parameters: pH, hydrogen peroxide concentration and Steel scrap content. The composites with high steel scrap content were effective to adsorb colour and COD in textile wastewater, and the adsorptive capacity increased with the superficial iron concentration. These steel scrap was also used as heterogeneous Fenton catalyst and had the advantage of being effective at pH 3.0 with a consumption of H_2O_2 lower than required by the homogeneous Fenton process.

Keywords: *Heterogeneous Catalyst, Textile dyeing wastewater, Adsorption, Hydrogen peroxide*

1. INTRODUCTION

The textile industry produces large volumes of effluents that contain appreciable quantities of organic compounds which are not easily amenable for 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. Alternative solutions to the conventional treatment have been reported, including electrochemical treatment, ozonation and other advanced oxidation processes, such as heterogeneous photocatalysis or Fenton reagent. 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]. The primary oxidant in Fenton's reagent is the hydroxyl radical ($OH\cdot$) generated by the reaction of hydrogen peroxide with ferrous ion. However, despite the high efficiency, the process is limited by the acidic pH required (pH 2-4) and the high amount of sludge in the coagulation step [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].The leaching and deactivation of catalysts are still challenges for developing advantageous catalyst for oxidation of wastewaters.

Effective heterogeneous catalysts for Fenton oxidation are also suitable for adsorptive filtration [1,14].The adsorptive filtration is an innovative approach for the removal of contaminants from the liquid phase where toxic compounds are attached to a thin layer of iron oxide that has been immobilized on the surface of an appropriate filter medium, such as sand grains [14].The modification of the filtration matrix allows the simultaneous sorption of soluble contaminants, as well as the removal of the particulate material for filtration. Adsorption techniques have been widely applied to the

treatment of industrial wastewater containing dyes, heavy metals, and other inorganic and organic impurities [6]. In some cases, it is possible to recover the adsorbed dye through desorption and to reuse the large amounts of water employed by textile industries [8]. Activated carbon has been widely used for this purpose because of its high adsorption capacity. However, its high cost sometimes tends to limit its use. Several nonconventional, low-cost adsorbents have also been tried for dye removal; some of them are peat [6], barro branco lutite [8], bottom ash [10], activated rice husk [11], red mud [12], carbon slurry [13,14], cyclodextrin-based material [15], activated slag [16], wheat husk [17,18], and de-oiled soya [19]. In this work, the treatment of textile dyeing wastewater has been studied by adsorption and simultaneous catalytic wet hydrogen peroxide oxidation using a new composite steel scrap/H₂O₂.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Chemicals and Reagents

The chemical used throughout this study was analytical grade (make: Merck) hydrogen peroxide (30 % w/v, Merck). The double distilled water was used to prepare experimental solution. The pH of the solution was adjusted using 1N H₂SO₄ and 1N NaOH.

2.1.2 Steel Scrap

The steel scrap, the waste during metal sawing in the steel workshop was washed with double distilled water to remove the dust and calcined at 200°C for 2 hours. 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 steel scrap was used as an adsorbent. The adsorbent steel scrap was characterized through the determination of its specific Brunauer-Emmett-Teller (BET) area and iron content. The steel scrap has presented high capacity for removal of iron dissolved in water (15, 16). The morphologic analysis and mapping of the elementary composition of steel scrap was determined by scanning electron microscopy and Energy dispersive X-ray spectroscopy (SEM / EDX).

2.1.3 Characterization of Textile Dyeing Wastewater

The textile dyeing wastewater samples were collected from an equalization tank in a textile industry at Tirupur, Tamilnadu, India. Samples were then preserved in the

refrigerator at 4°C in accordance with the standard methods for the Examination of Water and Wastewater (APHA, 2002). The wastewater samples were characterized for pH, Biochemical Oxygen Demand (BOD_{3,27°C}), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Chlorides, and Sulphate concentrations as per the Standard Methods. The characteristics of raw effluent are listed in Table 1.

Table 1: Characteristics of the Raw Textile Dyeing Effluent

Sl.No.	Characteristics	Unit	Value
1	Color, Absorbance	436 nm	0.707
		525 nm	0.574
		620 nm	0.416
2	Chemical Oxygen Demand	mg/L	1788
3	pH	-	8.14
4	Chlorides	mg/L	396
5	Biochemical Oxygen Demand, 3day, 27°C	mg/L	780
6	Sulphate	mg/L	450
7	Total suspended solids	mg/L	50
8	Total dissolved solids	mg/L	3410

2.2 Methods

The capacity of adsorption of the steel scrap was determined experimentally by contacting the wastewater with different dosages of steel scrap 10 g/L to 60 g/L at pH 3, 4, 5, 6 and 7. The conical flasks of capacity 250 ml were shaken for 6 h at room temperature using a shaker at 90 rpm. Afterwards the liquid was drained for determination of the remaining BOD₃, COD and colour.

The adsorption and simultaneous heterogeneous Fenton oxidation were carried out using different dosages of steel scraps, in the range 10 g/L to 60 g/L and hydrogen peroxide concentration in the range of 10 ml/L-20 ml/L, at different initial pH. Blank tests using only H₂O₂ were also performed and the results showed that a negligible degradation occurs by the oxidation with hydrogen peroxide only.

In a typical run, 250 ml of textile wastewater was added to the reactor together with the steel scrap. The mixture was agitated for 15 min at 90 rpm and the pH was adjusted to the desired value using 1N H₂SO₄. Then, H₂O₂ was added to achieve the desired H₂O₂ concentration and the mixture was agitated at 90 rpm for 120 min. After the treatment, the samples were centrifuged at 3000 rpm for 5 min and the liquid was analyzed in order to determine the

residual hydrogen per oxide concentration, COD and colour.

2.3 Analysis

The textile wastewater samples were analysed for pH, Biochemical Oxygen Demand, Chemical Oxygen Demand, Total Dissolved Solids, Total Suspended Solids, Chlorides, and Sulphate concentrations as per the Standard Methods (21). The Table 2 shows the details of the analytical methods and instruments used for different parameters. In Table 3, the instruments used for determination of the characteristics of the steel scrap are presented.

Table 2: Characteristics and Method of Analysis

Sl.No.	Characteristics	Analytical Method	Instrument/ Equipment used
Textile Dyeing Effluent			
1	Colour	Spectro Photometric method	UV-Vis spectrophotometer
2	COD	Dichromate digestion method	COD digestion Flask
3	pH	Potentiometry method	pH meter (197,WTW,Germany)
4	Chlorides	Argentometric method	Burette,Pipete
5	BOD, 3day,27°C	Winkler's method	BOD incubator
6	Sulphate	Barium Sulphate method	UV-vis spectrophotometer
7	Total suspended solids	Gravimetric method	Oven, Balance
8	Total dissolved solids	Gravimetric method	Oven, Balance

Table 3 Steel Scrap Characterization

Sl.No	Characteristics	Instrument/Model
1	Scanning electron microscope (SEM)	Philips XL-30 Hitachi Model-S-400
2	Energy dispersive X-Ray Analysis (EDX)	Philips XL-30 Hitachi Model-S-400
3	Brunauer-Emmett-Teller (BET)	Micromeritics Instrument Model ASAP2020

3. RESULTS AND DISCUSSION

3.1 Chemical and textural characterization of Steel scrap

The textural characteristics of steel scrap are summarized in table.4. The solids presents a small surface area with a wide pore sizes distribution.

Table 3: Characterization of the Steel Scrap

Sl.No	Parameter	Unit	Value
1	BET surface area	m ² /g	0.5192
2	Micropore volume	cm ³ /g	1.8 x 10 ⁻³
3	Micropore width	nm	3.1
Pore size distribution			
4	Micro	%	54.8
5	Meso	%	17.2
6	Macro	%	28
7	Point of zero charge		6.5-7.9

3.2 Chemical Composition and Morphologic Analysis of Steel Scrap

The chemical composition of the steel scrap is shown in Table 5. 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. The (Energy Dispersive X-Ray) EDX analysis showed presence of very high amount of Fe, C and O as shown in Figure 2.

Table 5: Chemical Composition of the Steel Scrap 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

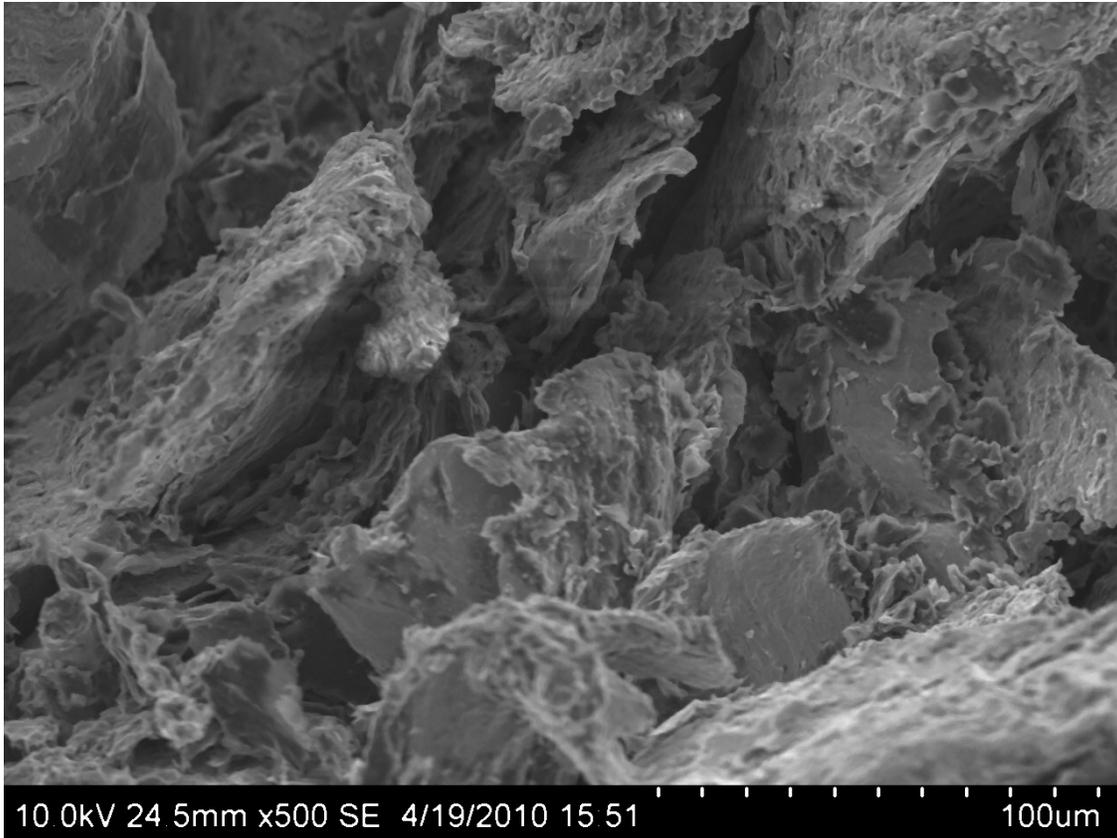


Fig. 1: Morphologic Analysis of Steel Scrap used as Catalyst

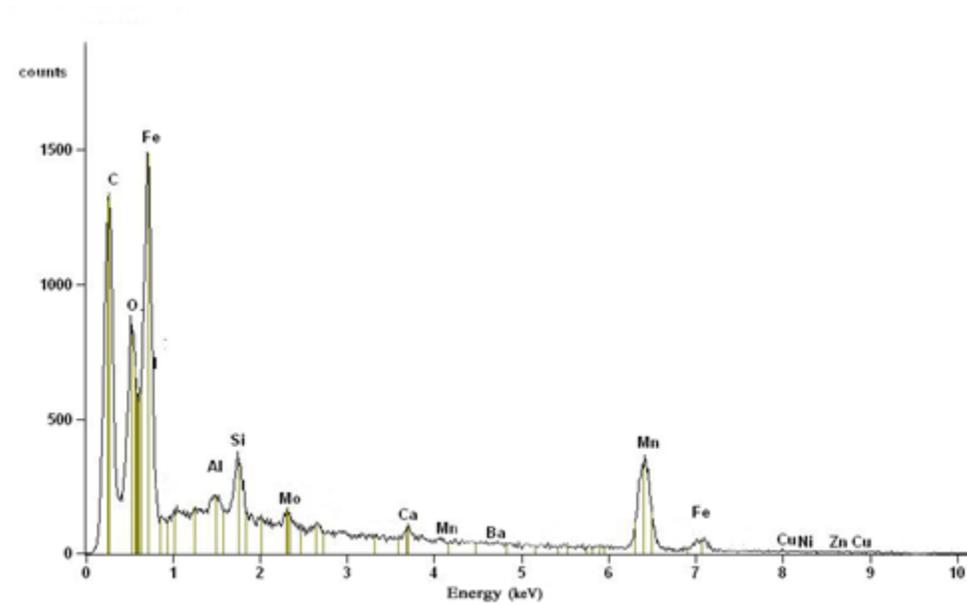


Fig 2: EDX Analysis of the Steel Scrap used as Catalyst

3.2 Textile dyeing wastewater adsorption on to Steel scrap

The contact of the effluent with the steel scrap for 6 h at a room temperature of 27°C at a pH of 8.14 and with

different dosage of steel scraps showed the colour and COD removal of 96% at 620 nm and 69% respectively as shown in Figures 3 and 4.

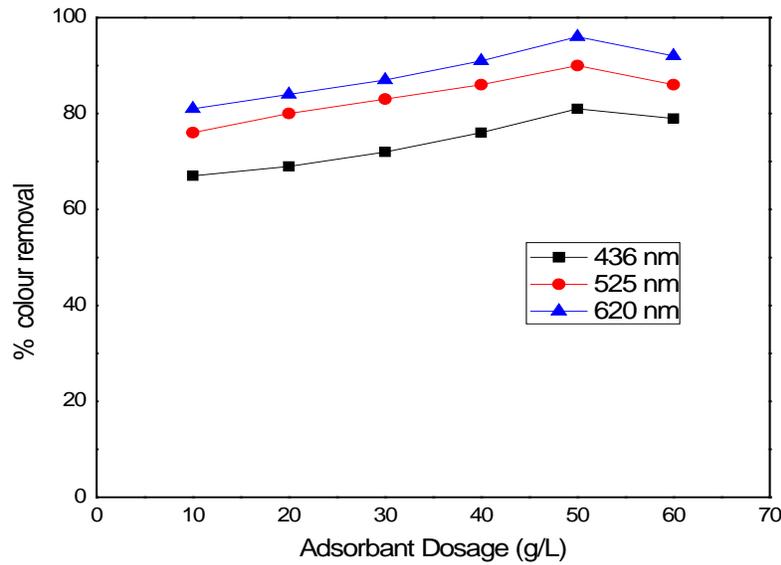


Fig 3: Effect of Steel Scrap Dosage as Adsorbent On Color Removal

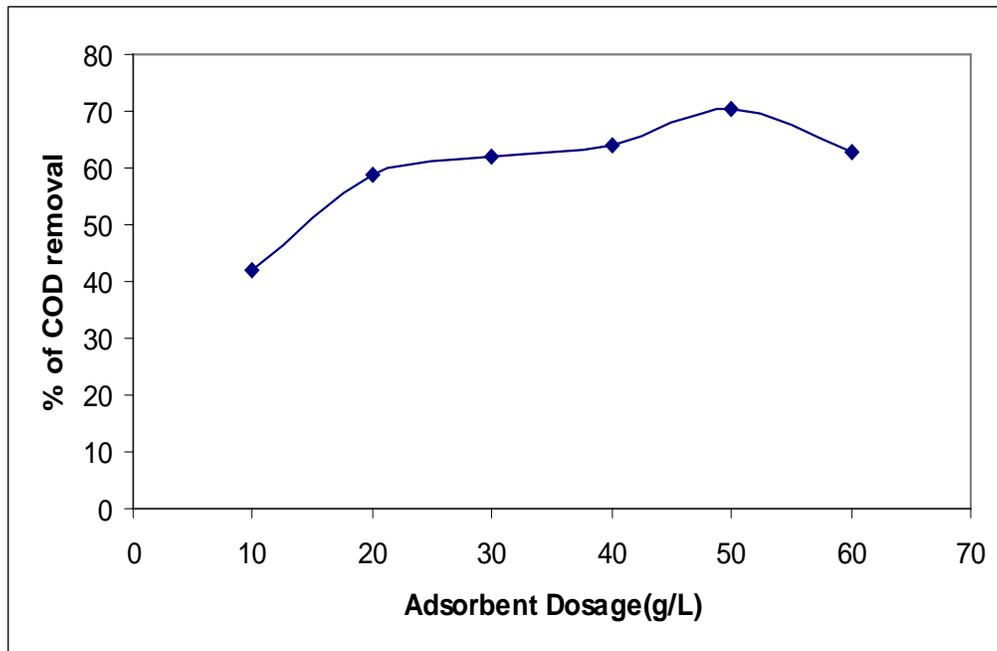


Fig 4: Effect of Steel Scrap Dosage as Adsorbents on COD Removal

The adsorptive capacity of the steel scrap depends on the iron oxide content. Iron oxide aggregates have special characteristics in aqueous solution and are present as ferrihydrite in a gelatinous and insoluble coverage on the adsorbent carbon surface with high adsorptive capacity. [22]

The effect of the pH on the adsorptive capacity of the steel scrap was evaluated in the range 3 – 8 as shown in Fig.5. The COD removal is nearly independent of the initial pH.

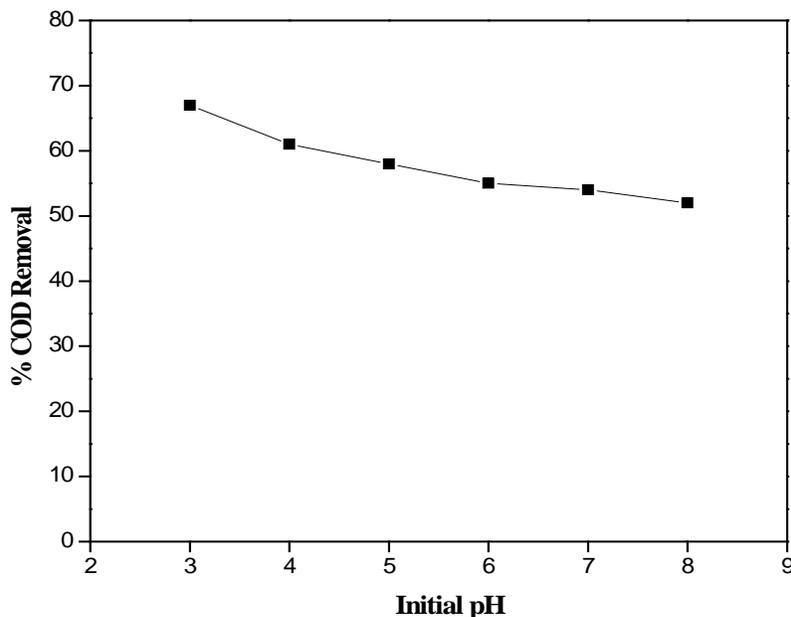


Fig.5: Effect of the Initial pH on the COD Removal by Adsorption

3.4 Kinetics of COD Removal by Heterogeneous 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 dyeing wastewater by heterogeneous Fenton oxidation could be expected.

The kinetics of COD removal by heterogeneous Fenton oxidation was studied using 50 g / L of steel scrap catalyst at a initial pH of 3 as shown in Fig.6. 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 [23] and can be explained by considering the fact that the hydrogen peroxide 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 oxidized iron on the solid's surface produced in the first stage could react with hydrogen peroxide 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.

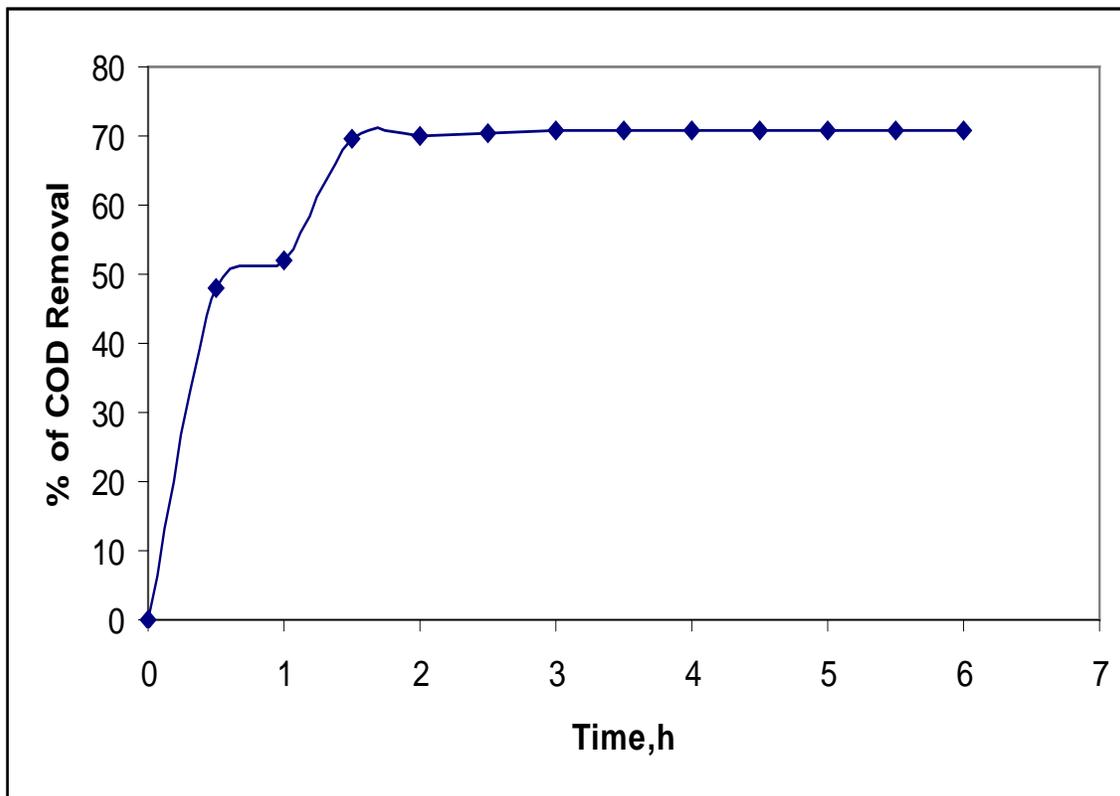
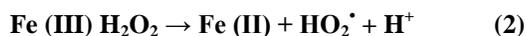
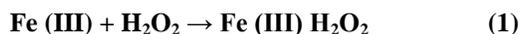


Fig 6: Kinetics of COD Removal by Heterogeneous Fenton Reaction using Steel Scrap as Catalyst

The kinetics of hydrogen peroxide disappearance was also evaluated during the textile dyeing wastewater degradation. The mechanism of H_2O_2 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^\bullet) 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 peroxide (Equation.1) is much faster than that of the others (9).

The hydroxyl radicals (OH^\bullet) formed in Equation.3 could oxidize organic compounds present in the textile wastewater (Equation 4) or react with hydrogen peroxide 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 50 g/L (Fig.7)

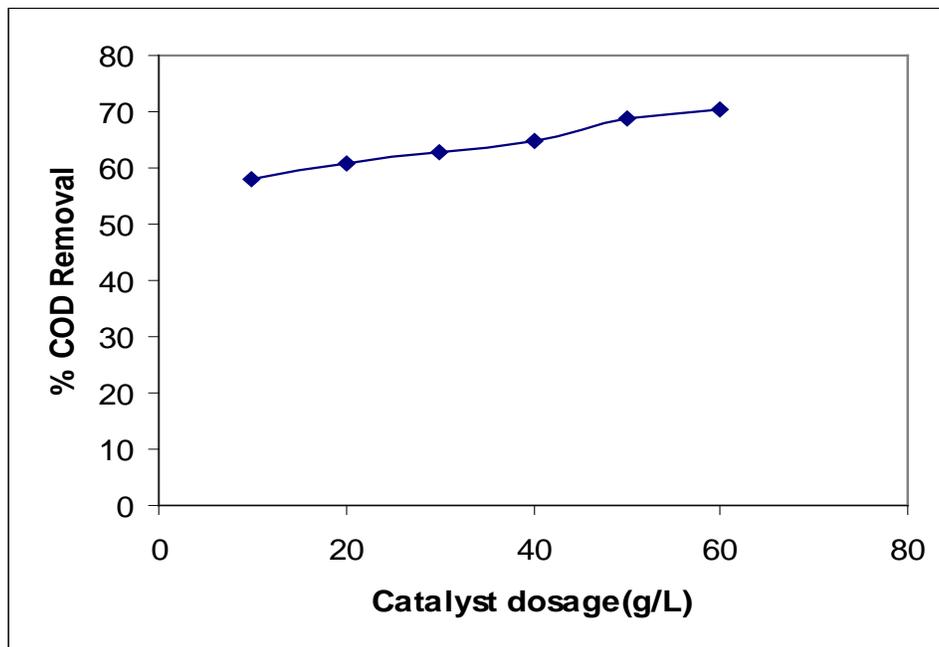


Fig 7: Effect of steel scrap dosage on COD removal by heterogeneous Fenton Oxidation (H₂O₂ = 15 ml/L, pH = 3, Reaction time = 1h, T=27°C)

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 homogenous 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 dyeing wastewater by heterogeneous Fenton reaction

It was previously reported (23) that the enhancement in the hydrogen peroxide concentration from 10 ml/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 H₂O₂ concentration was necessary to achieve 71% of COD removal using steel scrap.

As shown in Equation (1) – (6), 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 (Equation (7)).

$$[\text{Fe}^{\text{III}} \text{H}_2\text{O}_2] = [\text{Fe}^{\text{III}}]_{\text{T}} \frac{K_a [\text{H}_2\text{O}_2]}{1 + K_a [\text{H}_2\text{O}_2]} \quad (7)$$

The equilibrium constant for the adsorption of hydrogen peroxide on the solid's surface is

defined by equation (8)

$$K_a = \frac{[\text{Fe}^{\text{III}} \text{H}_2\text{O}_2]}{[\text{Fe}^{\text{III}}][\text{H}_2\text{O}_2]} \quad (8)$$

And the concentration of iron sites (free or occupied) is given by Equation (9).

$$[\text{Fe}^{\text{III}}]_{\text{T}} = [\text{Fe}^{\text{III}} \text{H}_2\text{O}_2] + [\text{Fe}^{\text{III}}] \quad (9)$$

When the iron sites are saturated with hydrogen peroxide, further increase of the hydrogen peroxide in the aqueous phase does not increase the formation of hydroxyl radicals, and consequently, it does not increase the oxidation of organic compounds in the wastewater.

The maximum COD removal achieved in the treatment of the same textile wastewater by homogeneous Fenton oxidation is nearly 65% using H₂O₂ concentration of 15 ml/L at pH 3.0 [23]. The heterogeneous Fenton oxidation using steel scrap as catalyst achieved 71% COD removal at room temperature using H₂O₂ concentration lower than 15 ml/L, and presented the additional advantage of being less sensitive to pH than the homogenous process.

4. CONCLUSIONS

The steel scrap can be used in the treatment of textile dyeing wastewater by heterogeneous catalyst in the Fenton reaction. The adsorptive capacity of the steel scrap increases as the superficial iron oxide content increases. The treatment of textile wastewater using the 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 leached to the aqueous phase indicating that the homogeneous Fenton reaction was not important and the catalyst is quite stable.

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