CHAPTER 4
RESULTS AND DISCUSSION

4.1 INTRODUCTION

This chapter presents the results pertaining to the degradation of textile and pharmaceutical effluents by sonochemical, Fenton’s oxidation and sorption processes. In the present study, the degradation was accelerated by using different hybrid processes, such as, sono-sorption (SS), sono-Fenton (SF) and sono-Fenton-sorption (SFS). The mechanism and kinetics of different processes were studied and the results are discussed in this section in detail.

4.2 DEGRADATION USING SONOLYSIS, FENTON’S OXIDATION AND SORPTION

4.2.1 Activation of Tea Waste

The influence of activation of tea waste on the reduction of COD was studied and the results are shown in Figure 4.1. Without pretreatment, the maximum COD reduction observed was 9.09%. Little higher maximum COD reduction (13.64%) was obtained when tea waste was activated using NaOH. The reduction was little more (18.18%) for the formaldehyde pretreated and also for ultrasonically activated tea waste. Generally it is known that ultrasound will produce higher activation compared to chemical pretreatment.
In the present study, similar trend was observed in the case of ultrasound and NaOH pretreated tea waste, whereas the reduction observed for HCHO pretreated activated tea waste was similar to that of ultrasonically pretreated.

The maximum COD reduction (22.73%) was observed with the tea waste activated using sequential pretreatment i.e. HCHO followed by ultrasound (US). This may be due to the synergic effect of HCHO and US and moreover, the surface was activated simultaneously by chemical and mechanical means through HCHO and US, respectively. This treatment produces numerous micropores on the surface of the sorbent, which was confirmed from SEM images obtained (discussed later). The COD reduction of 20.45% was obtained when the sequential pretreatment using NaOH followed by US was employed.

![Figure 4.1](image)

Figure 4.1 Effect of different tea waste activation methods on maximum COD reduction. (Conditions: Effluent volume : 100 mL; Initial COD: 30667 mg/L; sorbent dosage: 6 g/L ; temperature: 30 °C; pH : natural (5.0))
To confirm the best pretreatment method, the surface characterization using Boehm titration was performed and the results are presented in Table 4.1. The ultrasound produced very little changes on the surface group of tea waste.

**Table 4.1  Boehm titration of surface groups on tea waste before and after different pretreatment methods**

<table>
<thead>
<tr>
<th>Tea waste pretreatment method</th>
<th>Basic groups (mmol/g)</th>
<th>Acidic groups (mmol/g)</th>
<th>Carboxylic (mmol/g)</th>
<th>Phenolic (mmol/g)</th>
<th>Lactonic (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before pretreatment</td>
<td>0.179</td>
<td>0.251</td>
<td>0.123</td>
<td>0.119</td>
<td>0.009</td>
</tr>
<tr>
<td>US</td>
<td>0.186</td>
<td>0.259</td>
<td>0.127</td>
<td>0.121</td>
<td>0.011</td>
</tr>
<tr>
<td>HCHO</td>
<td>0.209</td>
<td>0.344</td>
<td>0.156</td>
<td>0.147</td>
<td>0.041</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.311</td>
<td>0.21</td>
<td>0.089</td>
<td>0.111</td>
<td>0.01</td>
</tr>
<tr>
<td>HCHO+US</td>
<td>0.215</td>
<td>0.349</td>
<td>0.113</td>
<td>0.191</td>
<td>0.045</td>
</tr>
<tr>
<td>NaOH+US</td>
<td>0.318</td>
<td>0.214</td>
<td>0.087</td>
<td>0.114</td>
<td>0.013</td>
</tr>
</tbody>
</table>

The increment in COD reduction after US treatment was due to the mechanical effect of ultrasound. When the tea waste was pretreated with HCHO, better increment on surface acidity group was observed, whereas when tea waste was pretreated with NaOH, better increment on surface basicity group was observed. This increase in surface group enhanced the sorption capacity of tea waste.

The sequential treatment of HCHO followed by US, and NaOH followed by US, produced better enhancement in surface groups compared to other pretreatments. So, it can be concluded that when tea waste was pretreated by HCHO followed by US, the enhancement of COD reduction was due to the increase in surface groups produced by HCHO and the mechanical
effect caused by US on the surface of tea waste. Further, SEM analysis (discussed later) also showed the presence of numerous micropores on the surface of the tea waste after activation, which is highly required for the better adsorption of pollutants. Hence further sorption related experiments were performed with the tea waste activated by HCHO followed by US.

### 4.2.2 Degradation using US Alone

The textile and pharmaceutical effluents were individually subjected to ultrasound irradiation and the effect of sonication time on % COD reduction was studied and the results obtained are shown in Figure 4.2. The COD reduction obtained for textile effluent after 180 min of sonication was 39.13% (Figure 4.2a).

The effect of sonication time on % COD reduction for pharmaceutical effluent is shown in Figure 4.2b. The COD reduction was found to increase with an increase in sonication time and after 180 min, 20.31 % COD reduction was obtained.

In sonolysis, the COD reduction was due to acoustic cavitation, which involves a process of formation, subsequent growth and implosion of bubbles filled with vapor and/or gas. When these bubbles collapse explosively, the temperature and pressure in the bubbles can reach up to several thousand Kelvin and several hundred atmospheres respectively (Dahlem et al 1998; Suslick 1990).
Figure 4.2 Effect of time on % COD reduction during sorption, sonolysis and Fenton process. a) textile effluent, b) pharmaceutical effluent. (Conditions: Effluent volume : 500 mL; initial COD : 29333 mg/L (textile) and 10667 mg/L (pharmaceutical); initial pH : 3.0 for Fenton’s process and 5.0 for sonolysis and sorption, sorbent dosage : 6 g/L (for sorption))
Under these extreme conditions, the organic recalcitrants were degraded through two different mechanisms: 1) pyrolytic decomposition of organics and water molecules; 2) hydroxyl radicals generated due to the decomposition of water molecules oxidize the organic pollutants present in bulk liquid, as shown below. In these reactions, ‘((‘))’ denotes the ultrasonic irradiation.

\[
\begin{align*}
H_2O + \text{•}H + \text{•}OH & \quad (4.1) \\
O_2 + \text{•}O & \quad (4.2) \\
\text{•}H + O_2 & \rightarrow \text{•}OOH \quad (4.3) \\
\text{•}O + H_2O & \rightarrow 2 \text{•}OH \quad (4.4) \\
\text{•}H + O_2 & \rightarrow \text{•}OH + \text{•}O \quad (4.5) \\
2 \text{•}OH & \rightarrow H_2O_2 \quad (4.6) \\
2 \text{•}OOH & \rightarrow H_2O_2 + O_2 \quad (4.7)
\end{align*}
\]

These highly reactive hydroxyl radicals are transferred to the bubble interface and then to the bulk solution, which promote the degradation of organic compounds. It has been proved that hydrophilic compounds with low vapor pressures were effectively destroyed in bulk solution by an oxidative degradation using hydroxyl radicals produced during bubble collapse. The hydrophobic compounds with high vapor pressures undergo thermal decomposition inside the bubbles (Liang et al 2007). In the present study, as real effluent was employed, the effluent might contain different organic pollutants that are hydrophilic or hydrophobic in nature. Thus, in sonolysis, the COD reduction might be due to both the mechanisms.
During sonolysis, the generated hydroxyl radicals will recombine to produce H$_2$O$_2$ (Equation 4.6) which is detrimental to the degradation of organic pollutants. In this work, the production of H$_2$O$_2$ during sonolysis of textile and pharmaceutical effluent was found to be very less (65 and 80 µM respectively, after 180 min). This is due to the fact that the chance of hydroxyl radical reacting with organic pollutant might be much higher than that of recombination, as the concentration of the organic pollutant is very high.

It has been reported that at very high frequency of irradiation, the rarefaction and compression cycle during sonication become too short to permit the molecules to be pulled apart sufficiently to produce a bubble. The time span of implosion and number of hydroxyl radicals regenerated decrease with an increase in frequency (Hamdaoui and Naffrechoux 2009). Thus the use of low frequency ultrasound makes the treatment process effective.

The higher operating cost associated with sonication restricts its large scale industrial applications. So, it is required to couple other effective oxidative process with sonication to minimize the operating cost as well as to obtain better performance.

Therefore, in the present study, two different hybrid oxidative processes were proposed. In the first one, ultrasound was coupled with Fenton’s process and sorption. In the second method, sonolysis was coupled with dual oxidant system (DOX).

4.2.3 Fenton Process and Sorption Studies

The treatment of textile effluent by Fenton’s process showed lesser COD reduction compared to sonolysis and the reduction was about 27.27%
The treatment of pharmaceutical effluent using Fenton’s process at an initial pH 3 showed around 14.06 % COD reduction after 180 min, which is also comparatively lesser than that of sonolysis. When the Fenton’s process was carried out at effluents’ natural pH (5.0), COD reduction obtained was 18.18 and 9.38% for textile and pharmaceutical effluent, respectively. The decrement in COD reduction is due to the fact that, above pH 3, the ferrous sulfate precipitates as Fe(OH)$_3$ (Ghodbane and Hamdoui 2009a).

In Fenton’s process, the reaction between Fe$^{2+}$ and H$_2$O$_2$ generates hydroxyl radicals, which are non selective and highly reactive. These radicals degrade the organic recalcitrants present in the effluent. The well established mechanism of Fenton’s process is shown below:

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO} + \text{OH}^- \quad (1.6)$$

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{OOH} + \text{H}^+ \quad (4.8)$$

$$\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (4.9)$$

The concentrations of Fe$^{2+}$ and H$_2$O$_2$ were found to decrease with time during Fenton’s process as both were continuously consumed to produce hydroxyl and other radicals (Equations 1.6, 4.8 – 4.9). At the end of Fenton’s process (after 180 min), the residual concentration of Fe$^{2+}$ and H$_2$O$_2$ was found to be 6 and 50 mg/L, respectively for textile effluent while for pharmaceutical effluent the values were found to be 0.02 and 0.4 g/L, respectively. The lesser concentration of H$_2$O$_2$ was also attributed to very little recombination of hydroxyl radicals. Since the concentration of the effluent was very high, the hydroxyl radicals produced were utilized for oxidation purpose.
Sorption using activated tea waste produced lesser COD reduction compared to Fenton’s process and sonolysis. After 180 min contact time, the sorption showed 22.73 and 12.5% COD reduction for textile and pharmaceutical effluents, respectively. As can be seen from the Figure 4.2, initial rate of COD reduction observed with sorption was high compared to other processes. However, as the time increases, the rate was found to decrease. The rapid sorption observed during first 30 min was attributed to two factors viz., availability of higher number of vacant active sites during the initial phase and the presence of high concentration gradient between adsorbate and adsorbent surface.

The observed results clearly indicated that the activated tea waste, which is a cost effective and waste material, could be employed successfully to remove pollutants. Uddin et al (2009) explored the potentiality of tea waste for the successful removal of methylene blue.

4.2.4 Sono-Sorption (SS) and Sono-Fenton Process (SF)

The sono-sorption was carried out using activated tea waste as sorbent. The effect of time on % COD reduction of textile and pharmaceutical effluent for different processes is shown in Figure 4.3.

When the sorption was performed in the presence of US, 77.27% COD reduction was observed for textile effluent. When it was treated with sorption and sonication, the COD reduction observed was 22.73 and 39.13% respectively. The treatment of pharmaceutical effluent with SS produced 43.75% COD reduction whereas COD removal obtained with sorption and sonication for pharmaceutical effluent was 12.5 and 20.31%, respectively.
Figure 4.3  Effect of time on % COD reduction during sono-sorption (SS), sono-Fenton process (SF) and sono-Fenton-sorption (SFS). a) Textile effluent and b) pharmaceutical effluent (Conditions: [Fe(II)] = 50 mg/L for textile effluent and 0.3 g/L for pharmaceutical effluent, and [H₂O₂] = 400 mg/L and 3 g/L respectively for textile and pharmaceutical effluents, during Fenton related processes, [sorbent] = 6 g/L for sorption related processes, initial pH = 3.0 for Fenton related processes and 5.0 for sorption, initial COD : 29333 mg/L (textile) and 10667 mg/L (pharmaceutical)).
The drastic increase in COD reduction with sono-sorption may be due to the synergistic effect of US and sorption. In the presence of ultrasonic irradiation, the large molecules of organic pollutants were converted into smaller molecules by pyrolytic decomposition and oxidation (Liang et al 2007). In addition, the presence of solids in sonication changes the dynamics of cavitation bubbles and produce high speed jet of liquid called micro jet (Thompson and Doraiswamy 1999). These micro jets may reach velocity more than 100 ms\(^{-1}\) (Mason 1991) to produce pitting and erosion.

In addition, high pressure shock waves and acoustic vortex micro-streaming were also produced during sonication. These actions enhanced the pore diffusion and mass transfer across the boundary layer (Hamdaoui and Naffrechoux 2009). Further, acoustic streaming caused due to ultrasound waves improved the mass transfer (Nouri and Hamdaoui 2007) and made the pores present in the sorbent available for sorption.

Further, the reduction in sorbent size was normally observed due to ultrasound irradiation. This was due to the breakage of solid particles. This breakage has two benefits on the degradation: decrease in particle size enhances the surface area, which is very much required for better sorption; and breakage leads to increase in number of solid particles. The presence of more fine particles enhances the nucleation site, thus accelerating the sonolytic degradation. The results observed in the present study are in accordance with previous studies (Entezari and Soltani 2009; Entezari and Soltani 2008; Entezari and Al-Hoseini 2007; Sonawane et al 2008).

The SF treatment of textile effluent for 180 min showed 63.64% COD reduction, whereas for pharmaceutical effluent, 48.44% COD reduction was observed. The treatment using Fenton process showed 27.27 and 14.06% COD reduction for textile and pharmaceutical effluent, respectively. For both
the effluents, the rate of degradation during SF process was found to be much higher than sonolysis and Fenton’s process.

The enhancement in COD reduction is due to synergistic effect of sonolysis and Fenton process. During Fenton and Fenton-like reactions, Fe$^{3+}$ was continuously generated, which further reacts with H$_2$O$_2$ to form a complex intermediate, Fe-O$_2$H$^{2+}$ (Equation 1.8). This intermediate will spontaneously decompose into Fe$^{2+}$ and OOH but the rate of decomposition was much slow (Pang et al 2011). The continuous decrease of H$_2$O$_2$ due to this reaction will reduce its availability, which makes Fenton’s reaction slow.

$$Fe^{3+} + H_2O_2 \rightarrow Fe-O_2H^{2+} + H^+ \quad (1.8)$$

The accumulation of less reactive intermediate can be prevented using ultrasound irradiation. In the presence of US, this intermediate was very rapidly decomposed to produce Fe$^{2+}$ (Equation 4.10) (Pang et al 2011), which is very much required for Fenton’s reaction. Hence the residual Fe$^{2+}$ concentration was found to be little higher in SF process (12 mg/L for textile effluent while it was about 0.05 g/L for pharmaceutical effluent) compared to that of Fenton’s process (6mg/L for textile effluent while it was about 0.02 g/L for pharmaceutical effluent). This is due to enhanced generation of Fe$^{2+}$ by the application of ultrasound.

$$Fe-O_2H^2+ \rightarrow Fe^{2+} + OOH \quad (4.10)$$

The comparison between SS and SF for the treatment of pharmaceutical effluent illustrated that during first 60 min of degradation, SS was found to be an attractive treatment process, which produced better COD removal (35.94%) compared to that of SF (31.25%). After 180 min of treatment, the COD reduction obtained with SS and SF was almost closer. This is attributed to the fact that sorption occurred at rapid phase in the
presence of ultrasound during the initial period that led to better reduction in residual COD. After 60 min, non-availability of active sites restricted the sorption phenomena thereby further COD reduction was completely contributed by the US alone. This trend was not found during textile effluent degradation in which sono-sorption was found to be the better option from beginning to end of the process, compared to that of sono-Fenton process.

The effect of sorbent dosage, particle size and initial pH on % COD reduction was investigated for sono-sorption. These studies were not extended to sono-Fenton process as no sorbent was employed. Further, the effect of initial pH was not studied for sono-Fenton process as the increase in pH beyond 3 precipitate the iron as iron oxide.

4.2.4.1 Effect of Adsorbent Dosage

The effect of adsorbent dosage on COD reduction during the treatment of textile and pharmaceutical effluent by SS was studied and the results are shown in Figure 4.4. The COD reduction observed for 2, 4, and 6 g/l of adsorbent dosage after 180 min was 54.5, 68.18 and 77.27% respectively for textile effluent, whereas, the reduction observed for pharmaceutical effluent was 31.25, 39.06 and 43.75% respectively. The results showed that the COD reduction was increased with an increase in sorbent dosage and this may be attributed to the fact that the increase in dosage increased the availability of more adsorption sites. Similar results were reported by Entezari and Al-Hoseini (2007) and Uddin et al (2009).

The other important effect due to the presence of sorbent is the increase in cavitation bubbles due to the supply of crevices and the wall of solid particle plays a vital role in producing tiny bubbles with a promotion of jet towards the wall. The wall of the particle may easily break the spherical
symmetry of the large sized cavitation bubbles, which produced large amount of tiny cavitation bubbles.

![Figure 4.4](image)

**Figure 4.4** Effect of sorbent dosage on % COD reduction during sono-sorption. (Conditions: Effluent volume : 500 mL; initial COD : 29333 mg/L (textile) and 10667 mg/L (pharmaceutical); Initial pH – natural; Ultrasound - 30 kHz; process time: 180 min.)

The increase in cavitation bubbles accelerated the production of oxidant radicals during their collapse, which in turn affected the degradation positively. Keck et al (2002) reported that the addition of inert particles during sonication doubles the reaction rate. On the other hand, Nakui et al (2007) investigated the role of coal ash on the intensification of phenol degradation in the presence of US and concluded that the presence of inert particles increased in nucleation sites for cavitation bubble due to their surface roughness. Similar results were reported by Tuzziuti et al (2005).
4.2.4.2 Effect of particle size

The effect of activated tea particle size on COD reduction was studied keeping other parameters as constant and its effect on the degradation is shown in Figure 4.5. It was observed that the decrease in particle size increased the COD reduction.

![Effect of sorbent size on % COD reduction during sono-sorption](image)

**Figure 4.5** Effect of sorbent size on % COD reduction during sono-sorption. (Conditions: Effluent volume : 500 mL; natural pH (5.0); sonication time: 180 min; frequency: 30 kHz; sorbent dosage: 6 g/L, surface area : 10.27, 14.84 and 21.02 m²/g for 250-354, 177-250 and 80-120 μm particles, respectively.)

The sorbent size has two major effects; the decrease in particle size increases the surface area, which increases the adsorption rate and increase in number of particles will create more nucleation sites. For larger particles, the diffusion resistance to mass transport is higher (Dogan et al 2009) and most of the internal surface of the particle may not be utilized for sono-sorption, which reduces the efficiency.
The size of the sorbent before and after the sono-sorption of textile effluent was analyzed to find out the changes occurred on its size due to ultrasound irradiation. It was found that the amount of tea waste, which has lost its original size was about 8% for the size range 80-120 µm, whereas the effect was insignificant (<3%) for larger particles (177-250 and 250-354 µm).

The results showed that the ultrasound irradiation produced more breakage on smaller size particles compared to larger size particles. It should be noted that these particles were already exposed to ultrasound (with same frequency) during pretreatment. The breakage of sorbent particles enhanced the surface area and in turn increased the adsorption rate. In addition, increase in number of particles enhanced the number of nucleation sites that accelerated sono-degradation.

The specific surface area of activated tea waste before and after sono-sorption was found to be 21.02 m²/g and 11.13 m²/g, respectively. The decrease in surface area clearly indicates the occurrence of sorption on tea waste. Similar trend was observed with pharmaceutical effluent.

### 4.2.4.3 Effect of initial pH

The influence of initial pH of the effluent (textile and pharmaceutical) on COD reduction by sonolysis, sorption and sono-sorption was studied. In order to investigate the initial pH, it is apt to analyze the initial degradation rate than the final one, since the pH changes as the reaction proceeds. The COD reduction profiles obtained as a function of initial pH of the textile effluent for sonolysis, sorption and sono-sorption are shown in Figure 4.6a.
Figure 4.6  Effect of initial pH of the effluent on % initial COD reduction during sorption, sonolysis and sono-sorption. a) textile effluent b) pharmaceutical effluent. (Conditions: Effluent volume : 500 mL; initial COD : 29333 mg/L (textile) and 10667 mg/L (pharmaceutical); sonication time : 30 min; frequency: 30 kHz; Sorbent dosage (for sorption and sono-sorption): 6 g/L)
The results showed that the initial COD reduction was higher (25%) for sonolysis at pH 1. The initial COD reduction observed at pH 2, 3, 4, 5, 6 and pH 8-10 was 20.5, 18.2, 15.9, 13.6, 9, and 4.5% respectively.

Similar studies were performed with pharmaceutical effluent and the results obtained are shown in Figure 4.6b. The maximum initial COD reduction for pharmaceutical effluent (10.94%) was obtained at extreme acidic conditions (pH 1-2). The degradation was found to decrease with an increase in initial pH and the increase in pH beyond 5 did not affect the COD reduction.

Higher rate of degradation occurred at acidic conditions in sonolysis and this may be due to the occurrence of more protonation and pyrolysis at acidic conditions (Jiang et al 2002; Lin et al 1996). The enhancement in degradation rate under acidic conditions can also be attributed to the higher rate of formation/accumulation of hydroxyl radicals, which enhanced the degradation of organic pollutants (Wang et al 2005; Priya and Madras 2006).

At pH 5-10, the initial COD reduction was found to be very less compared to acidic conditions. This is due to the lower concentration of hydroxyl radicals at this condition and the other aspect is that only about 10% of the hydroxyl radicals that are generated in the bubble can diffuse into the bulk liquid (Ghodbane and Hamdaoui 2009b). In addition, at pH 5 – 8, a larger number of hydroxyl radicals recombine to form H₂O₂ that leads to decrease in hydroxyl radical concentration (Ghodbane and Hamdaoui 2009b). Similar trends were observed for the ultrasonic degradation of many organic pollutants, such as methyl orange, azo dyes, and nitro phenol (Jiang et al 2002; Lin et al 1996; Ince and Guyer 2004).
In sorption, the initial COD reduction observed for textile effluent was 4.55% at extreme acidic conditions (pH 1-2), whereas at pH 3-4, the initial COD reduction was 9.09%. Higher initial COD reduction (18.18%) was observed at pH 5 and similar reduction was observed at neutral and basic conditions. The same trend was observed for the pharmaceutical effluent.

In sono-sorption, the initial COD reduction observed for textile effluent at pH 1 was 27.27% and it was decreased gradually to 18.18% when the pH was increased to 4. Thereafter, the reduction was increased to 27.27% when the pH was increased to 5. The initial COD reduction was nearly same (22.73%) in the pH range 6–10. The initial reduction of COD was higher at acidic condition (pH 1) and decreased when the pH was increased from pH 2 to 4. When the pH was increased beyond 4, significant increase in reduction was observed.

The results observed showed that the contribution due to sonolysis was very less when the pH was above 6. Therefore, the COD reduction was found to remain constant in the pH range 6-10.

On the other hand, 28.13% COD reduction was observed for the pharmaceutical effluent at an initial pH of 1 during sono-sorption and further increase in initial pH decreased the COD reduction and this trend was noticed till pH 3 (23.44%). At pH 4, maximum COD reduction (28.13% similar to pH 1) was achieved beyond which it was found to be comparatively less (around 21%)

The pH of the solution affects the surface charge of the adsorbent as well as the degree of ionization of the different pollutants present in the effluent (Uddin et al 2009; Wang and Zhu 2005). The change in pH affects the adsorptive process through dissociation of several functional groups on the adsorbent surface active sites.
In the present study, the PZC of the activated tea waste was found to be 4.6. When the actual pH was greater than PZC, the surface of the tea waste may get negatively charged due to the adsorption of hydroxyl radicals and also the carboxyl group present on the surface of the tea waste may get deprotonated thereby producing negatively charged adsorption sites. Therefore, when the pH was greater than 4.6, the negatively charged radicals especially hydroxyl radicals were repelled by the active sites (negatively charged) and thus, all the hydroxyl radicals are available for the degradation. In addition, the positively charged pollutants present in the effluent got adsorbed easily on the negatively charged active sites. Thus, at initial pH 5, higher COD reduction was observed.

In sono-sorption, after 180 min, the COD reduction observed at an initial pH of 5 for textile effluent was 90.91%, whereas at neutral conditions (pH 6-8), the COD reduction was 86.36%. The COD reduction obtained at basic conditions after 180 min was 81.82%. Thus, it can be concluded that pH 5 was found to be the optimum pH for better degradation of textile effluent during sono-sorption. For pharmaceutical effluent also, the optimum pH was found to be 5. The effect of initial pH on COD reduction was not investigated for SFS process as all the Fenton related experiments were conducted with initial pH of 3.

4.2.5 Sono-Fenton-Sorption

In Fenton system, reaction between ferrous ions and hydrogen peroxide produces hydroxyl radicals, which are strong oxidizing agents. Ferrous sulfate will produce Fe$^{3+}$ in acidic medium and Fe$^{3+}$ will in turn react with H$_2$O$_2$ to produce an intermediate Fe-OOH$^{2+}$. In the presence of ultrasound, the rate of decomposition of this less reactive intermediate to Fe$^{2+}$ and $\cdot$OOH was significantly enhanced. The Fe$^{2+}$ reacts with H$_2$O$_2$ and
produced hydroxyl radicals again and a cycle mechanism was established (Song and Li 2009).

It can be observed from Figure 4.3a that the textile effluent COD reduction was higher (90.91%) after 180 min for SFS compared to sonosorption (77.27%) and sono-Fenton (63.64%). Blank experiment was conducted to analyze the effect of Fenton process alone and the COD reduction observed was 27.27%.

The COD reduction observed for pharmaceutical effluent after 180 min (Figure 4.3b) was 71.88% and the rate of degradation was found to be much higher than individual processes. This clearly demonstrated the intensification of COD removal due to the simultaneous use of ultrasound, Fenton and sorption. This intensification was attributed to several factors, such as, simultaneous production of hydroxyl radicals through ultrasound and Fenton`s reaction, pyrolytic degradation of organic recalcitrants by sonolysis, enhanced sorption due to surface pitting caused by ultrasound and better mass transfer provided by ultrasound.

The enhancement in SFS may be attributed to the factors, such as, enhanced production of hydroxyl radicals, decomposition of organic pollutants by pyrolysis due to US and combined effect of sonolysis, sorption and Fenton reaction. The effect of initial effluent concentration, Fe(II) and H₂O₂ dosage, addition pattern of iron on % COD reduction during SFS was studied and the results obtained are discussed below.

4.2.5.1 Effect of initial concentration

To investigate the effect of initial concentration of the effluent, it is appropriate to analyze initial degradation rate. In this work, three different
concentrations of textile effluent (13333, 20000 and 29333 mg/L) and pharmaceutical effluent (3500, 7000 and 10666.67 mg/L) were selected to study the effect of initial concentration. For textile effluent, the COD reduction observed after 30 min of SFS treatment for 13333, 20000 and 29333 mg/L of initial concentration were 30, 33.33 and 50% respectively. For pharmaceutical effluent, the values corresponding to 3500, 7000 and 10666.67 mg/L of initial concentration were found to be 23.81, 35.71 and 40.63%, respectively.

This clearly showed that the increase in initial concentration increased the initial rate of COD reduction for both the effluents. This is attributed to the fact that in the absence of any organic pollutants, highly reactive hydroxyl radicals simultaneously produced by ultrasound and Fenton’s reagent will recombine to produce $\text{H}_2\text{O}_2$. Therefore, the increase in organic pollutant concentration increased the hydroxyl radicals’ attack on pollutant, which in turn increased the oxidative degradation. In addition, the life-span of hydroxyl radicals is very short (only a few nanoseconds) (Daud and Hameed 2010). Increase in concentration enhanced the probability of collision between the organic pollutant and hydroxyl radicals, which led to enhancement in degradation.

Madhavan et al (2010) reported similar results for the degradation of ibuprofen in aqueous environments using US. During sorption, the increase in organic pollutant concentration enhanced the concentration gradient, which increased the rate of sorption. The driving force for diffusion is very important for adsorption process and the increase in adsorbate concentration resulted in increase in the driving force (Dogan et al 2009).

4.2.5.2 Effect of Fe(II) dosage

The effect of Fe(II) dosage on textile effluent COD reduction is shown in Figure 4.7a and the COD reduction observed for 40 mg/L and
Figure 4.7  Effect of Fe(II) dosage on % COD reduction during sono-Fenton-sorption. a) textile effluent b) pharmaceutical effluent. (Conditions: Effluent volume : 500 mL; initial COD : 29333 mg/L (textile) and 10667 mg/L (pharmaceutical); sorbent dosage : 6 g/L; H$_2$O$_2$ dosage : 500 mg/L; initial pH : 3, temperature: 30 °C; frequency: 30 kHz; sonication time : 180 min).
50 mg/L of Fe(II) was 86.4 and 90.9 % respectively but for 60 mg/L Fe(II), the COD reduction observed was 81.82%.

The increase in % COD reduction when the concentration was increased from 40 to 50 mg/L may be due to the enhanced production of hydroxyl radicals that are responsible for oxidizing the organic pollutants. Further increase in Fe(II) concentration reduced the COD reduction, which is due to self quenching of hydroxyl radicals (Equation 4.6) that decreased the concentration of both Fe(II) and hydroxyl radicals.

Similar studies were performed for pharmaceutical effluent in which the COD removal was found to increase from 67.19 to 71.88% when the dosage of Fe(II) was increased from 0.1 to 0.3 g/L. Further increase in Fe(II) dosage showed a drastic reduction in % COD removal.

This reduction might be due to the hydroxyl radical scavenging effect of excess iron through undesirable reaction (Equation 4.9), which decreased the COD reduction. Ghodbane and Hamdaoui (2009a) analyzed the effect of addition of Fe(II) on degradation of Acid blue 25 and reported the similar trend.

4.2.5.3 Effect of H$_2$O$_2$ dosage

The influence of H$_2$O$_2$ dosage on % COD reduction for both the effluents was studied and the results obtained are shown in Figure 4.8. It can be observed from Figure 4.8a that the maximum COD reduction was observed with 400 mg/L for textile effluent and the increase or decrease in concentration beyond the optimum value decreased the COD reduction. The increase in % COD reduction with an increase in H$_2$O$_2$ concentration may be attributed to the decomposition of H$_2$O$_2$ into hydroxyl radicals at high temperatures and pressures (Wu et al 2001).
Figure 4.8  Effect of H$_2$O$_2$ dosage of on % COD reduction during SFS.  
(a) textile effluent  b) pharmaceutical effluent. (Conditions:  
Effluent volume : 500 mL; sorbent dosage : 6 g/L; Fe(II)  
dosage : 50 mg/L (for textile), 0.3 g/L (for pharmaceutical);  
initial COD : 29333 mg/L (textile) and 10667 mg/L  
(pharmaceutical); initial pH: 3, temperature: 30 °C;  
frequency: 30 kHz; sonication time: 180 min, initial pH: 3).
The decrease in COD reduction when the dosage was increased beyond the optimum value may be due to the detrimental effect which occurred at higher concentrations of H$_2$O$_2$.

At higher concentrations, the recombination reaction of hydroxyl radicals was more predominant and H$_2$O$_2$ itself acted as the hydroxyl scavenger (Equation 4.11), which lowered the availability of the hydroxyl radicals for the degradation process (Ghodbane and Hamdaoui 2009a).

\[
\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2\cdot/\text{O}_2\cdot + \text{H}_2\text{O}
\]  

(Equation 4.11)

Figure 4.8b shows the % COD removal with respect to different initial concentrations of H$_2$O$_2$ at an initial pH of 3 and Fe(II) concentration of 0.3 g/L for pharmaceutical effluent. The H$_2$O$_2$ dosage had significant effect on COD reduction and % COD removal was found to increase from 60.94 to 71.88% when its dosage was increased from 1000 to 3000 mg/L. Beyond 3000 mg/L, COD reduction was found to decrease slightly (70.31% for 4000 mg/L) and this may be due to the intrinsic scavenging effect of hydroxyl radicals (Equation 4.11), which produced much less reactive species, such as, HO$_2$· and/or O$_2$·.

Teo et al (2001) reported that the increase in concentration of H$_2$O$_2$ increased the initial rate of degradation of 0.4 mM of p-chlorophenol with an increase in H$_2$O$_2$ concentration from 0 to 20mM but further increase in H$_2$O$_2$ concentration to 40 mM showed a marginal effect on the degradation. Furthermore, the increase in concentration beyond 40 mM decreased the rate of degradation.

4.2.5.4 Effect of addition pattern of iron

The effect of addition pattern of iron on % COD reduction during SFS was studied. For textile effluent, when the iron was added in a single dose, COD reduction was found to be 95.5% after 180 min. On the other
hand, when the iron was added in small doses at regular intervals, a little enhancement in COD reduction (97.73%) was observed. This is attributed to the fact that in a single dose addition pattern, the excessive presence of iron during initial phase of reaction affects the oxidation process. This problem will not be there in sequential addition, as the presence of small amount at all times makes the degradation process more effective.

For pharmaceutical effluent, sequential addition produced 81.25% COD reduction while single dose produced 71.88% COD reduction. The change in pattern of iron addition produced a significant effect in pharmaceutical effluent degradation whereas the impact was very less in the case of textile effluent. This is because, already over 95% COD reduction was achieved with single dose Fe(II) addition and further degradation is very difficult due to the presence of the pollutants which might be recalcitrant to this method.

4.2.6 Biodegradability Analysis

The biodegradability of the wastewater was analyzed to study the performance of different methods investigated. The BOD₅/COD ratio of untreated textile effluent was 0.31. After sonication for 180 min, the ratio was found to be 0.45. The biodegradability after sorption, Fenton process, sono-Fenton and sono-sorption treatment of textile effluent was found to be 0.37, 0.42, 0.55 and 0.60 respectively. The biodegradability was enhanced to 0.71 in SFS process. This shows that the hybrid methods made wastewater more biodegradable and the maximum enhancement was observed with SFS due to the combined effect of sonolysis, Fenton reaction and sorption process. It also shows that after SFS process, the effluent can be easily treated using biological methods.
Similar study was extended to pharmaceutical effluent to estimate the effluent quality after different treatment processes. The biodegradability index (BOD$_5$/COD) of the untreated effluent was found to be 0.127. After sonication for 180 min, the index was raised to 0.153. After sorption, Fenton’s oxidation, sono-Fenton and sono-sorption, the index was observed to be 0.141, 0.143, 0.224 and 0.208 respectively. Comparatively high biodegradability index of 0.4 was achieved using SFS process.

When compared to textile effluent, SFS produced significantly lesser enhancement in the biodegradability index of pharmaceutical effluent. This clearly depicts that it is difficult to treat pharmaceutical effluent biologically even after SFS. It shows the presence of biorefractory complex organic compounds in the treated effluent.

### 4.2.7 Reusability of Adsorbent

Repeated adsorption/desorption cycles were performed to examine the reusability of adsorbent in SFS process. After 180 min of SFS, the COD reduction observed for textile effluent in first, second and third cycles was 95.5, 86.36 and 72.73% respectively. On the other hand, the COD reduction observed for pharmaceutical effluent was 71.88, 65.63 and 57.81% respectively, during first, second and third cycles of adsorbent.

The % COD reduction was found to decrease as the number of cycles increased. This may be due to the damages occurred on the binding sites and morphological changes on the surface. The continuous pitting on the surface of the adsorbent contributes to the morphological changes. Under ultrasonic irradiation, the violent explosion of bubbles near the surface caused micro jets which produced non symmetrical shock waves that cause pitting on the surface.
4.2.8 Adsorption Mechanism

In liquid-solid adsorption, three major consecutive steps involved are transport of adsorbate molecules from the bulk liquid to the external surface of the adsorbent by diffusion through liquid boundary layer, diffusion from the external surface into the pores of the adsorbent (intra-particle diffusion) and adsorption of diffused pollutants on the active sites present in the internal surface of the pores. The last step is usually very rapid as compared to the first two steps. Hence, the determination of rate controlling step is restricted to only two steps (step 1 and 2). Therefore, the overall rate of adsorption is controlled by either liquid film or intra-particle diffusion or by both.

The intra-particle diffusion coefficient (K_w) values obtained for textile effluent were 142.8, 1696.0 and 2304.0 mg/(L.min) for sorption, sono-sorption and SFS respectively. It can be observed that the intra-particle diffusion coefficient obtained for sono-sorption was much greater than the values obtained in the absence of US (sorption process). The results show that the incorporation of US enhanced the intra-particle diffusion by nearly 12 times.

On the other hand, the K_w values were found to be 176.68, 529.69 and 741.19 mg/(L.min) for sorption, SS and SFS respectively during the degradation of pharmaceutical effluent. The results clearly showed that the incorporation of ultrasound enhanced the pore diffusion and hence the value of K_w was improved significantly (2.99 times). The turbulence caused by the microstreaming (that is generation of tiny eddies produced by sound waves) enhanced the mass transfer at the interface between solid and liquid and also within the pores. In addition, micro-jets with very high velocities developed in the bulk solution intensified the convective mass transfer inside the pores.
The intra-particle diffusion coefficient was still higher for sono-Fenton-sorption process. This is due to the fact that, highly reactive hydroxyl radicals were produced simultaneously through ultrasound and Fenton reagent. The complex pollutant molecules were oxidized by the hydroxyl radicals produced to simpler molecules. In addition, under the influence of ultrasound irradiation, pyrolysis also made the larger pollutant molecules to smaller molecules. Moreover sonolysis also increased the turbulence and in turn mass transfer. This enabled the pollutants to diffuse easily through the pores and hence the intra-particle diffusion coefficient was enhanced considerably compared to other methods.

The values of liquid film mass transfer coefficient \( (k_sA) \) obtained for textile effluent were \( 3 \times 10^{-6}, 6 \times 10^{-6} \) and \( 10 \times 10^{-6} \m^3/\text{min} \) during sorption, sono-sorption and SFS respectively. The \( k_sA \) value obtained for pharmaceutical effluent during sorption, SS and SFS was found to be \( 1 \times 10^{-5}, 5 \times 10^{-6} \) and \( 8 \times 10^{-6} \m^3/\text{min} \), respectively. This result clearly shows that the presence of ultrasound during sorption process enhanced the liquid film coefficient drastically. This enhancement may be attributed to the extreme conditions generated during the violent collapse of bubbles in the bulk liquid. The symmetric collapse was hindered when the bubble was collapsed near the solid surface and thus the bubbles will collapse asymmetrically. These asymmetrical collapses in a heterogeneous system produced the micro jets with higher velocity.

In addition, these symmetric and asymmetric collapses generate high pressure shock waves, which cause turbulence at the interface of liquid solid; thereby the rate of mass transfer increased near the solid surface. In addition with high speed micro jets and shockwaves, the sonication also produced acoustic vortex micro streaming (Adewuyi 2001; Vasanthakumar
et al 2008, Spahn and Schlunder 1975), which enhanced the mass transfer into the bulk solution as well as in the boundary layer (Vasanthakumar et al 2008).

Higher $k_s A$ values were observed for SFS compared to sono-sorption. This is due to the fact that, as explained earlier, the combination of sonication and Fenton process produced numerous highly reactive hydroxyl radicals and also increased the turbulence, which offered higher values.

4.2.9 Adsorption Kinetics

4.2.9.1 Langmuir-Hinshelwood kinetics

Langmuir-Hinshelwood (L-H) kinetics is the most commonly used kinetic model to analyze heterogeneous reactions. The initial concentration of the organic pollutant is an important parameter in wastewater treatment processes. It was observed that the initial rates were increased with an increase in initial concentration. The best linear fit obtained between inverse of initial rate and inverse of initial concentration as shown in Figure 4.9 explains that the initial rates were well followed the L-H kinetics.

For textile effluent, the limiting rate constant of reaction at maximum coverage under the given experimental conditions ($k_r$) value was found to be $1.77 \times 10^{-2}$ and $2.56 \times 10^{-2}$ min$^{-1}$ for sono-sorption and SFS, respectively. The equilibrium constant for the adsorption of the substrate on sorbent ($K$) value was $3.02 \times 10^{-5}$ and $3.38 \times 10^{-5}$ L/mg for sono-sorption and SFS, respectively. On the other hand, the value of $k_r$ for pharmaceutical effluent was found to be $1.23 \times 10^{-2}$ and $1.82 \times 10^{-2}$ min$^{-1}$ for SS and SFS respectively. The value of $K$ was $1.44 \times 10^{-4}$ and $1.52 \times 10^{-4}$ L/mg for SS and SFS respectively.
Figure 4.9 Variation of the inverse of the initial rate versus the inverse of the initial COD. a) textile effluent, b) pharmaceutical effluent.
Higher values of L-H parameters were obtained for SFS compared to that of SS. The higher values obtained for SFS indicate that the effective degradation was achieved due to the synergistic effect of ultrasound, sorption and Fenton’s process. On the other hand, the experimental results obtained during sonolysis and SF process did not fit with the L-H model satisfactorily. This is due to the fact that, this model is more suitable only for heterogeneous system. Further, high values of L-H kinetic constants were obtained for textile effluent compared to pharmaceutical effluent. This indicates that the SFS could degrade textile effluent effectively.

4.2.9.2 Adam-Thomson Relation

The initial adsorption kinetic coefficient can be determined using Adam-Thomson relation (Hamdaoui and Naffrechoux 2009). The values obtained for sorption, sono-sorption and SFS with respect to the treatment of textile effluent were 2.27 x 10^{-8}, 4.54 x 10^{-8}, and 7.38 x 10^{-8} L/(g.min), respectively and the values obtained for pharmaceutical effluent were 4.37 x 10^{-8}, 13.0 x 10^{-8}, and 18.1 x 10^{-8} L/(g.min), respectively.

The results showed that the incorporation of US doubled the value during textile effluent degradation while it was nearly tripled in the case of pharmaceutical effluent. The coefficient was still higher for sono-Fenton-sorption process in both the cases. Hydrodynamic effects induced by the sonication promote a significant increase in mass transfer across the boundary layer (Hamdaoui and Naffrechoux 2009). The enhancement of mass transfer across the liquid film may be due to the reduction in thickness of laminar boundary layer by the micro scale turbulence created by ultrasound.

4.2.10 Electrical Energy Consumption

It is highly required to compare the different treatment processes in terms of electrical energy consumption as it accounts a major fraction on
operating cost in the treatment of industrial wastewaters. The ‘Figure-of-merit’ electrical energy per order (EE/O) has been used to compare the energy efficiency of different processes.

In textile effluent degradation, the EE/O was found to be 1208.631 kWh/m$^3$/order for sonolysis and 592.5 and 250.2 kWh/m$^3$/order for sono-Fenton and SFS respectively. In pharmaceutical effluent degradation, the value was found to be 2642, 905 and 358 kWh/m$^3$/order for sonolysis, sono-Fenton and SFS respectively.

It should be noted that EE/O was estimated using COD values of the effluent and not the concentration of the pollutant. This study clearly depicts the advantage of using sono-Fenton-sorption in terms of electrical energy consumption as the value of EE/O was found to be significantly less compared to sonolysis. This indicates that operating cost can be minimized through less electrical energy consumption when sonolysis was coupled with sorption and Fenton’s process, which is highly required for large scale applications. Higher value of EE/O obtained with sonolysis clearly indicated its energy ineffectiveness.

The results also indicate high energy requirement for the treatment of pharmaceutical effluent compared to textile effluent. This is due to the recalcitrant organics present in the pharmaceutical effluent.

4.2.11 **Surface Analysis**

The surface morphology of the sorbent was characterized using scanning electron microscopy (SEM) (Mogollon et al 1998) and Figure 4.10a shows the surface of the untreated sorbent, which contains rough and irregular layers that will enable sorption.
Figure 4.10 SEM micrographs of tea waste (a) untreated tea waste, (b) activated tea waste, and (c) tea waste after sono-Fenton-sorption process
The changes in the morphology of sorbent due to the pretreatment by formaldehyde followed by US are shown in Figure 4.10b. It could be seen that the sonicated sample exhibits patterns of uniform micropores on the surface of pretreated sorbent and it might be caused by two modes of caviational bubble collapse.

In the first mode, cavitational bubbles collapsed on the surface of the sorbent may cause direct damage by shock waves produced due to implosion. In the second one, the bubbles collapsed near the surface on the liquid bath caused microjets and these hit the surface of the sorbent, which produced non-symmetrical shock waves that caused pitting on sorbent surface. The sorbent with a majority of micro pores adsorbs molecules more readily.

The sorbent after sono-Fenton-sorption of textile effluent is shown in Figure 4.10c. The surface of the sorbent was completely covered by thick layer of adsorbate. The micropores present on the surface (appeared in Figure 4.10b) were not seen since they were occupied by sorbate molecules. Similar pitting effect was reported on iron surface due to US by Dai et al (2006).

In order to confirm the adsorption of pollutants on sorbent and to investigate the changes in surface functional groups, FTIR analysis and Boehm titration were carried out and results were discussed later.

4.2.12 FTIR analysis and Boehm Titration

4.2.12.1 Textile effluent

The FTIR spectra of activated tea waste before and after SFS of textile effluent are shown in Figure 4.11. The spectrum (Figure 4.11a) shows a number of absorption peaks, indicating the complex nature of the tea waste.
The broad trough at 3454 cm\(^{-1}\) indicates the hydroxyl stretching vibration band. The presence of amide was observed at 1633 cm\(^{-1}\). The band in the region 1300-1000 cm\(^{-1}\) may result from tertiary nitrogen species incorporated into the carbon structure (Zhang et al 2010). The presence of amide and nitrogen species in the tea waste may be attributed to their plant origin.

The spectra of tea waste after SFS of textile effluent are shown in Figure 4.11b. Several new peaks were observed on this spectrum which may be due to the adsorption of pollutants. It can be observed that the peaks in the
range of 3900-3400 cm\(^{-1}\) may be due to OH stretching of phenolic and hydroxyl group. The peaks in the range 1650-1600 cm\(^{-1}\) may be due to stretching vibrations of aromatic ring. The band around 1200-1100 cm\(^{-1}\) may be due to CO stretching vibrations of carboxylic and phenolic groups.

The peak around 800 cm\(^{-1}\) may be due to out of plane bending vibrations of aromatic compounds. A shallow peak was observed in tea waste after SFS at 563 cm\(^{-1}\). This low intensity peak may be due to the presence of Fe on the surface of the sorbent. So, it can be concluded that some amount of Fe either used or unused was adsorbed on the tea waste.

The surface acidity and basicity strengths of activated tea waste before and after SFS obtained through Boehm titration are presented in Table 4.2. The data showed that the amount of acidic and basic groups on the surface of the activated tea waste was increased significantly after use compared to before its use.

It clearly shows that different pollutants were adsorbed on the surface of the tea waste during SFS. In particular, significant increase in surface basicity groups was observed after SFS process. This may be due to the fact that the pH of the solution (effluent) was maintained at 3, as indicated earlier and the pH was well below PZC (pH = 4.6). Therefore, the surface might have more acidic groups which attracted negatively charged pollutants during the process. Thus, at the end of the process, more basic groups were present on the surface. The obtained data were well in accordance with FTIR spectra.

### 4.2.12.2 Pharmaceutical effluent

The FT-IR spectrum of the tea waste before and after SFS is shown in Figure 4.12. The broad trough present at 3454 cm\(^{-1}\) was attributed to hydroxyl stretching vibration band.
Figure 4.12 FT-IR spectra of activated tea waste: a) before use b) after its use on treatment of pharmaceutical effluent using sono-Fenton-sorption

The band appears in 1300 - 1000 cm$^{-1}$ might be caused due to the presence of tertiary nitrogen species incorporated into the carbon structure. A peak observed at 1633 cm$^{-1}$ may be due to the presence of amide. Figure 7b shows the FT-IR spectrum of tea waste after treatment in which several new peaks were found. The tertiary amines produced a doublet at 1125 cm$^{-1}$. Similarly, C-O stretching of phenol produced a sharp peak at 1277 cm$^{-1}$. A broad absorption seen at 3400 cm$^{-1}$ was due to O-H stretching of alcohols / phenols. The broad band at 770 cm$^{-1}$ arises from the out of plane bending of ring C-H bonds and a weak combination and overtone band appeared in the region of 2000-1650 cm$^{-1}$ confirmed the adsorption of aromatic hydrocarbons.
The C-O stretching (primary alcohol) was observed at around 1050 cm\(^{-1}\) and the stretching of R-C≡C (alkynes) caused a peak at 2140 cm\(^{-1}\). The shallow peak observed at around 560 cm\(^{-1}\) showed that the iron used in Fenton’s reagent was adsorbed either before or after its use.

The surface acidity and basicity strengths of activated tea waste before and after SFS in textile and pharmaceutical effluent obtained through Boehm titration are presented in Table 4.2.

**Table 4.2  **Boehm titration of surface groups on activated tea waste before and after sono-Fenton-sorption

<table>
<thead>
<tr>
<th>Activated tea waste</th>
<th>Basic groups (mmol/g)</th>
<th>Acidic groups (mmol/g)</th>
<th>Carboxylic (mmol/g)</th>
<th>Phenolic (mmol/g)</th>
<th>Lactonic (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before use</td>
<td>0.215</td>
<td>0.349</td>
<td>0.113</td>
<td>0.191</td>
<td>0.045</td>
</tr>
<tr>
<td>After its use in Textile effluent</td>
<td>0.796</td>
<td>0.655</td>
<td>0.219</td>
<td>0.331</td>
<td>0.105</td>
</tr>
<tr>
<td>After its use in pharmaceutical effluent</td>
<td>0.524</td>
<td>0.419</td>
<td>0.147</td>
<td>0.255</td>
<td>0.071</td>
</tr>
</tbody>
</table>

The enhancement in basic and acidic groups on the surface of activated tea waste after use compared to before use confirmed the adsorption of different pollutants present in the pharmaceutical effluent.

**4.2.13 Toxicity test**

Oxidative degradation of textile effluent may produce organic intermediates/final products, which are sometimes more toxic than the untreated effluent. To analyze the toxicity of effluent after SFS, disk diffusion
susceptibility test was carried out with *Escherichia coli*. Under similar conditions, the diameter of the inhibition zone was found to be 19 mm with respect to untreated effluent whereas it was 9 mm for the effluent treated with SFS process. These values are inclusive of disk diameter (6 mm). So it can be concluded that the hybrid method reduced the toxicity of the effluent.

For pharmaceutical effluent, the zone of inhibition was found to be 26 mm for untreated effluent whereas under similar conditions, it was about 10 mm for the effluent treated with SFS. This indicates the decrement in toxicity after the treatment with the method proposed. Higher values obtained with pharmaceutical effluent showed high toxicity compared to textile effluent which was attributed to the presence of harmful pharmaceutical molecules.

### 4.3 DEGRADATION USING DUAL OXIDANT SYSTEM WITH AND WITHOUT SONOLYSIS

The degradation of textile effluent using sonolysis showed 39.13% COD reduction (as said early) after 180 min. Under similar conditions, sonolysis showed about 20.31% COD reduction for pharmaceutical effluent. In order to improve the degradation efficiency and to minimize the operating cost, Fenton’s oxidation and sorption were coupled with sonolysis.

The proposed hybrid treatment (SFS) produced secondary pollutants, such as, iron sludge after Fenton’s process, and sorbent containing recalcitrant pollutants. Thus, it is necessary to treat these generated pollutants, which is time consuming and makes the technology cost ineffective.

In order to minimize the generation of sludge and to avoid secondary pollutants generation, in this study another novel hybrid oxidative treatment process viz., US coupled dual oxidant system (US/DOX), was
proposed. In this system, non-polluting oxidants, such as, hydrogen peroxide and ammonium persulfate were employed. In addition, iron swarf, a difficult to eliminate waste material was employed instead of conventional ferrous sulfate salt.

In persulfate oxidation, persulfate ions were oxidized to produce sulfate free radicals (Equation 4.12). To break the O-O bond in persulfate ions, necessary activation energy should be supplied through thermal or non-thermal methods. Earlier studies (Kolthoff and Miller 1951; Gupta and Gupta 1981) revealed that the activation energy requirement for thermal activation is 140.2 kJ/mol whereas it is about 61.96 kJ/mol when activation was performed using iron. Due to this fact, thermal activation was not used in this study; rather the persulfate activation was performed using iron and other non-thermal methods.

\[ \cdot O_3S-O-O-S-O_3^- \rightarrow 2 \cdot O_3S-O^* \]  

(4.12)

In this work, different methods were tested for the activation of persulfate oxidation.

**4.3.1 Effect of different activators**

The effect of three activators such as iron-swarf, ultrasound, and iron-swarf coupled with ultrasound on persulfate oxidation were tested. The best activator was arrived based on the % COD reduction obtained during the treatment of pharmaceutical effluent. Initially, the iron swarf was used as the activator. The presence of transition metal, such as, Fe$^{2+}$ activates persulfate (Equations 4.13 – 4.14) to achieve effective oxidation. Hoag (2000; 2002) reported that the effective use of persulfate, for environmental applications could be achieved using either heat or by the addition of Iron (II). The COD
reduction obtained for pharmaceutical effluent when iron-swarf was used as activator was found to be 10.49%.

\[
\text{Fe}_{\text{(Iron-swarf surface)}} + 2 \text{H}^+ \rightarrow \text{Fe}^{2+} \quad \text{(Under acidic condition)} \quad (4.13)
\]

\[
\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{2-} \quad (4.14)
\]

The use of ultrasound as activator during the treatment of pharmaceutical effluent showed 35.94% COD reduction. Under ultrasound irradiation, persulfate ions were cleaved by thermolytic action to produce sulphate ions. These sulfate ions may abstract hydrogen atom from water molecules to produce hydroxyl radicals (Equations 4.15 –4.16). Effective decomposition of persulfate and production of hydroxyl radicals showed better degradation by this method.

\[
\text{S}_2\text{O}_8^{2-} (\text{+}) \rightarrow 2 \text{SO}_4^{2-} \quad (4.15)
\]

\[
\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \cdot \text{OH} \quad (4.16)
\]

where, )))) denotes ultrasound.

The simultaneous use of these methods was tested and the maximum COD reduction (54.69%) was observed with ultrasound coupled iron-swarf activation of persulfate. Price and Clifton (1996) used ultrasound for activating the persulfate oxidation and reported that the application of ultrasound at 25°C produced the same rate of decomposition offered by thermal reaction at 55°C.
4.3.2 Degradation using DOX

The effect of DOX system on the degradation of both textile and pharmaceutical effluents was studied and the results are shown in Figure 4.13. The results showed 56.82 and 51.56% COD reduction for textile and pharmaceutical effluents, respectively after 180 min of reaction. The experiments carried out with these two oxidants individually showed 13.07% \((H_2O_2)\) and 9.09% (ammonium persulfate) COD reduction for textile effluent whereas for pharmaceutical effluent, these values were found to be 20.31 and 10.49% respectively.

Higher reduction with hydrogen peroxide compared to persulfate oxidation was due to the fact that sulfate radicals are more stable compared to hydroxyl radicals, which slow down the reaction towards organic pollutants (Devi et al 2009). In addition, less production of \(Fe^{2+}\) ions at pH 5 minimizes the cleavage of persulfate ion (Equations 4.13 – 4.14).

The higher degradation observed during DOX process was due to the synergistic effect of dual oxidants and Fenton like process on the degradation of effluents. The simultaneous use of two effective oxidants, such as, activated ammonium persulfate and hydrogen peroxide caused ‘aggressive oxidation’ of pharmaceutical effluent. Further, Fenton like reaction was expected to occur in DOX system due to the presence of iron-swarf and hydrogen peroxide.

In the present study, the basic purpose of using iron-swarf particle was to initiate the dissociation of persulfate to produce sulfate ions. But these iron particles catalyzed the hydrogen peroxide oxidation through hydroxyl radical generation.
Figure 4.13 Effect of reaction time on % COD reduction during Ultrasound (US), Dual oxidant system (DOX) and Ultrasound coupled with dual oxidant system (US/DOX). a) textile effluent and b) pharmaceutical effluent, (Conditions: initial pH: 5 (natural pH), initial COD : 29333 mg/L (textile) and 10667 mg/L (pharmaceutical); mixing rate: 200 rpm, (H₂O₂) = 5 g/L, (Ammonium persulphate) = 5 g/L and (Iron-swarf) = 4 g/L)
The expected reaction mechanism involved in Fenton like process using iron-swarf is given below.

\[
\begin{align*}
\text{Fe} \text{ (Iron-swarf surface)} + 2 \text{H}^+ & \rightarrow \text{Fe}^{2+} + \text{H}_2 \quad (4.17) \\
\text{Fe} \text{ (Iron-swarf surface)} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+}-\text{surface} \quad (4.18) \\
\text{Fe}^{2+}-\text{surface} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + 2 \cdot \text{OH} \quad (4.19) \\
\text{Fe} \text{ (Iron-swarf surface)} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + 2 \cdot \text{OH}^- \quad (4.20) \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^- \quad (1.6) \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \cdot \text{O}_2\text{H} + \text{H}^+ \quad (4.21) \\
\text{Fe}^{3+} + \cdot \text{O}_2\text{H} + \text{H}^+ & \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}_2 \quad (4.22) \\
\text{Fe} \text{ (Iron-swarf surface)} + \text{S}_2\text{O}_8^{2-} & \rightarrow 2 \cdot \text{SO}_4^{2-} + \text{Fe}^{2+} \quad (4.23) \\
\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} & \rightarrow \text{Fe}^{3+} + \cdot \text{SO}_4^{2-} + \cdot \text{SO}_4^{2-} \quad (4.24) \\
\text{Fe}^{3+} + \text{S}_2\text{O}_8^{2-} & \rightarrow 2 \cdot \text{SO}_4^{2-} + \text{Fe}^{2+} \quad (4.25) \\
\cdot \text{SO}_4^{2-} + \text{H}_2\text{O} & \rightarrow \cdot \text{SO}_4^{2-} + \cdot \text{OH} + \text{H}^+ \quad (4.26) \\
\text{Fe}^{2+} + \cdot \text{OH} & \rightarrow \text{Fe}^{3+} + \cdot \text{OH}^- \quad (4.9)
\end{align*}
\]

4.3.3 Degradation using US/DOX

The effect of sonication time on COD removal in the presence and absence of dual oxidant system was investigated for both the effluents and the results obtained are shown in Figure 4.13.

It can be seen that 97.73% COD reduction was obtained for textile effluent (Figure 4.13a) during US/DOX system, while in the absence of DOX
in this system, the degradation was found to be very less (39.13%). On the other hand, 96.88% COD reduction was observed for pharmaceutical effluent with US/DOX system (Figure 4.13b) while the removal was found to be very less (20.31%) when sonolysis alone was performed for a period of 180 min. These results clearly indicate the significant enhancement in COD removal with US/DOX process and this is attributed to several factors that are discussed below in detail.

The presence of iron-swarf particles made the system heterogeneous and this in turn makes sonication very effective. These solid particles provide additional nuclei for the cavitation which lead to enhancement of cavitational activity in the liquid bath. Presence of salt (ammonium persulfate) made better distribution of chemical compounds thereby local concentration was increased at reaction sites (Thompson and Doraiswamy 1999).

The physicochemical properties of effluent such as vapour pressure and surface tension were altered due to the presence of salts which induce more cavitation and in addition, more violent collapse of bubbles was resulted. Brotchie et al (2010) reported that the presence of salt during sonication inhibited the bubble-bubble coalescence thereby the size of the collapsing bubbles would be lowered, which leads to more violent explosion of cavities that intensified the degradation process.

The catalytic action of iron-swarf particles was dramatically enhanced under ultrasound irradiation. In homogeneous liquid bath, shape of the bubbles is theoretically symmetrical and remains in spherical shape till they get collapsed. Since the heterogeneous solution contains solid particles, cavities are prone to collapse near the solid surface. This leads to drastic change in dynamics of cavitation and asymmetrical collapse of bubbles that leads to the production of high speed jet of liquid known as micro-jet (Mason 1991).
The speed of the micro-jet reported was normally in the range of 100 m/s. These jets activate the solid particles by surface pitting and erosion. Further these micro-jets enhanced the rate of phase mixing and mass transfer. In addition, asymmetrical and symmetrical explosion of cavities generates shock waves and this produces extreme turbulent flow at the interface between solid and liquid that increases the rate of mass transfer near the solid surface (Hamdaoui and Naffrechoux 2009).

It should be noted that the addition of solid particles in wastewater is expected to remove the contaminants by adsorption. Therefore, in the present study, the adsorption of contaminants by iron swarf particles during the US/DOX process was analyzed. A blank experiment using iron swarf (4 g/L) was performed with 500 mL of textile and pharmaceutical effluents at 200 rpm. The results showed very meagre COD reduction (<3%) for both the effluents. This clearly shows that that the degradation of organic pollutant was mainly occurred through oxidative route and not by adsorption on iron swarf.

To determine the contribution of persulfate oxidation, US/DOX was performed in the absence of persulfate and iron-swarf. In this case, the COD reduction obtained for textile effluent was 54.54% after 180 min, whereas for pharmaceutical effluent, 40.63% COD reduction was observed.

Similarly to assess the contribution of hydrogen peroxide oxidation, US/DOX was performed without hydrogen peroxide. In this case, the COD reduction of 68.18 and 54.69% respectively were observed for textile and pharmaceutical effluents.

It clearly showed that higher COD reduction was achieved without hydrogen peroxide compared to the oxidation carried out in the absence of persulfate. These experiments clearly illustrate that the contribution of
persulfate oxidation was much higher than that of hydrogen peroxide. This is in contradiction of the result presented in the earlier section (degradation using DOX), in which persulfate oxidation produced less degradation compared to hydrogen peroxide oxidation, for both the effluents. The enhanced contribution of persulfate oxidation was attributed to sono-Fenton like process occurred in US/DOX.

4.3.4 Effect of Initial pH

The textile and drug manufacturing industries employ a variety of raw materials, which are sometimes seasonal. This causes drastic fluctuations in pH of the effluent. It is well established that the pH of the solution plays a dominant role in oxidative degradation. So it is required to study the changes in efficacy of oxidative processes with respect to different initial pH.

To investigate the role of initial pH, it is required to analyze initial degradation rate rather than final degradation rate. This is due to the fact that the formation of intermediates and products will alter the solution pH drastically. The influence of initial pH was studied for different systems and the results are shown in Figure 4.14.

In sonolytic degradation of textile effluent, the maximum COD removal of 18.18% was achieved at pH 1 and the increase in pH reduced the COD removal. For the pharmaceutical effluent, the maximum COD reduction (7.82 %) was observed at acidic conditions (pH: 1- 3) and the degradation was found to decrease with further increase in pH. At neutral and basic conditions, very less degradation was observed. This is due to the fact that the acoustic cavitation generally enhances the protonation and pyrolysis at highly acidic conditions (Jiang et al 2002; Lin et al 1996). Therefore, at pH 4-11, lesser degradation was observed due to the lower concentration of hydroxyl radicals.
Figure 4.14 Effect of initial pH on initial COD reduction during Ultrasound (US), Dual oxidant system (DOX) and Ultrasound coupled with dual oxidant system (US/DOX). a) textile effluent and b) pharmaceutical effluent. (Conditions: reaction time: 30 min, mixing rate: 200 rpm, \( \text{H}_2\text{O}_2 = 5 \, \text{g/L}, \) Ammonium persulphate = 5 g/L and Iron-swarf = 4 g/L)

In DOX process, 22.73% COD reduction was obtained for textile effluent at an initial pH 1 and the maximum degradation was observed at pH 3. Further increase in initial pH decreased the degradation process. Similar
trend was observed for pharmaceutical effluent, in which 15.63% COD reduction was observed at an initial pH 1 and maximum COD removal (17.19%) was obtained at pH 3. This is due to the fact that there is a direct involvement of H⁺ in the reaction at the extreme acidic conditions through vigorous generation of ferrous ions from swarf surface. These ferrous ions involve in degradation through two different ways: these ions act as activator for persulfate oxidation thereby increasing the production of sulfate ions and also participate in Fenton like reaction, which generated hydroxyl radicals. The less degradation observed at pH 1 was attributed to less availability of hydroxyl radicals at extreme acidic conditions due to hydroxyl radicals scavenging by H⁺ ions (Equation 4.27) (Ustun et al 2010).

\[ \cdot \text{OH} + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O} \]  

(4.27)

The results showed that, increase in initial pH beyond 3 decreased the degradation significantly. The less productive degradation beyond pH 3 was caused by several factors: (1) less oxidation potential of hydroxyl radicals at higher pH conditions (E° = 2.8 and 1.95 V/SHE at pH 0 and 14 respectively) (Ustun et al 2010); (2) lesser production of ferrous ions from iron surface at non-acidic conditions; (3) mass transfer resistance was developed significantly due to the precipitation of a passive film on the iron-swarf surface (10), which made iron-swarf inactive; and (4) at pH above 5, ferryl ions were generated by destroying ferrous ions (Equation 4.28) (Xu and Wang 2011), which are more selective and less reactive oxidants compared to hydroxyl radicals. Thus, the optimal pH for DOX system was arrived at 3.0.

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{FeO}^{2+} + \text{H}_2\text{O} \]  

(4.28)

In US/DOX system, the increase in initial pH decreased the degradation rate for both the effluents. This is due to the fact that both ultrasound and DOX individually produced higher COD reduction only at
acidic conditions. The combination of these two processes showed better effect with respect to variation in pH. The results showed slight increase in degradation from 37.5 to 40.63% when the initial pH was altered from 1 to 3.

Maximum COD removal at pH 3 was attributed to the enhanced generation of ferrous ions at iron-swarf surface and also enhanced protonation and pyrolysis due to the ultrasonic irradiation at acidic conditions. Further increase in pH (beyond pH 3) decreased the degradation and this may be due to the fact that the degradation was not favoured at neutral and basic conditions in both US and DOX when these processes were carried out individually.

The optimum initial pH was found to be 3 for US/DOX process. Further DOX and US/DOX related experiments were performed at an initial pH 3. The use of ammonium persulfate not only facilitated the oxidative degradation but also provided excess acidity, which is much required for better COD removal. This is an interesting observation because this reduces the amount of acid to be added to reduce the pH to 3. Moreover, sulphate ions are more acidic in nature, which might keep the reactant pH at acidic conditions.

4.3.5 Effect of Mixing Rate

The influence of mixing rate on the degradation of organic pollutants present in textile and pharmaceutical effluent was studied by varying the mixing rates from 0-200 rpm, keeping initial pH as 3. The results obtained are shown in Figure 4.15 and it can be observed that the influence of mixing rate was found to be significant in DOX process whereas it was not so in US/DOX process in both the cases.
In DOX, the increase in mixing rate increased the degradation. Very less degradation at no mixing (0 rpm) may be attributed to the settling of iron-swarf, which affected the generation of ferrous ions. This in turn affected the production of both sulfate and hydroxyl radicals.

![Figure 4.15](image)

**Figure 4.15** Effect of mixing rate on % COD reduction during DOX and US/DOX. a) textile effluent and b) pharmaceutical effluent

The increase in mixing rates produced turbulent flow, which reduced the mass transfer resistance.
On the other hand, this trend was not observed with US/DOX. Even at 0 rpm (no mixing), 93.18 and 85.94% COD reduction was observed with textile and pharmaceutical effluents, respectively and this is mainly due to the beneficial stirring effect of US, which prevents the deposition of iron-swarf particles. The optimum mixing rate for DOX and US/DOX was chosen as 200 and 100 rpm respectively for both effluents.

### 4.3.6 Effect of Iron Addition

The effect of iron-swarf addition on COD removal was investigated and the results obtained are shown in Figure 4.16. In DOX, less degradation was observed with textile (13.63%) and pharmaceutical effluent (21.88%) when no iron was used.

In this case, the complete contribution was provided by hydrogen peroxide oxidation and no significant persulfate oxidation was occurred due to the absence of iron or any other activator.

The degradation was found to increase with an increase in iron dosage and this trend was observed till the iron dosage was increased to 4 g/L for textile effluent and 3 g/L for pharmaceutical effluent, beyond which the degradation was found to decrease. The increase in COD reduction from 13.64 to 65.91% for textile effluent and 21.88 to 54.69% for pharmaceutical effluent clearly indicates the action of iron swarf as activator in persulfate oxidation and its active participation in Fenton like process.

The addition of iron swarf in excess decreased the degradation of both textile and pharmaceutical effluents. It may be due to the fact that the Fe$^{2+}$ might act as intrinsic scavenger for sulfate radicals, which destroyed the sulfate radicals (Equation 4.29).

\[
\text{SO}_4^{\bullet^+} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2\bullet^+}
\]  \hspace{1cm} (4.29)
Figure 4.16  Effect of iron-swarf dosage on % COD reduction during dual oxidant process (DOX) and ultrasound coupled with dual oxidant system (US/DOX). a) textile effluent and b) pharmaceutical effluent (Conditions: Initial pH: 3, initial COD: 29333 mg/L (textile) and 10667 mg/L (pharmaceutical); mixing rate: 100 rpm (US/DOX), 200 rpm (DOX), \( \text{H}_2\text{O}_2 = 5 \text{ g/L}, \text{Ammonium persulphate} = 5 \text{ g/L} \)
In US/DOX process, 75 and 71.88% COD reduction was obtained for textile and pharmaceutical effluents, respectively, in the absence of iron. This is because, even in the absence of iron, hydroxyl radicals were produced under sonication and persulfate oxidation was activated by ultrasound. It generates the sulfate ions and subsequently, hydroxyl radicals were produced.

Further it was observed that increase in iron dosage enhanced the degradation till 4 g/L for textile effluent and nearly complete degradation was achieved at 4 g/L. At 5 g/L, the COD reduction was found to be 90.15%. For pharmaceutical effluent, the maximum degradation was observed at 3 g/L (100%) beyond which the reduction was negatively affected. This is attributed to the fact that the presence of solid particles in excess might result in scattering the sound waves, which reduced the net energy transferred to the system and in turn caused detrimental effect to sonication (Gogate 2008). From the results, the optimum dosage of iron for textile effluent was arrived at 4 g/L, and 3 g/L for pharmaceutical effluent.

4.3.7 Effect of addition Pattern of Iron

In this work, two different iron-swarf addition patterns were employed in DOX and US/DOX processes to investigate their role on the degradation of pollutants. In the first method, iron swarf was added to the reaction mixture as a single dose (optimal dosage of 4 and 3 g/L for textile and pharmaceutical effluents, respectively) well before the reaction. In the second pattern, iron-swarf was added in sequential manner (iron-swarf was added at regular interval of time (15 min) and at each time dosage of 0.33 and 0.25 g/L was added during textile and pharmaceutical effluent treatment, respectively till amount of total iron was added.

In both DOX and US/DOX processes, sequential addition of iron-swarf produced good results. In DOX process, sequential addition produced
72.73 and 65.63% COD reduction for textile and pharmaceutical effluent, respectively, whereas single step addition showed 65.91 and 54.69% COD reduction, respectively.

In US/DOX process, complete COD removal was observed for both the effluents within 150 min when sequential addition was followed whereas single step addition showed complete removal after 180 min. This may be attributed to the fact that during the initial stage of reaction, presence of excess iron due to single dose addition caused detrimental effect on the degradation as the iron itself acts as intrinsic sulfate scavenger (Equation 4.29). The incremental addition of iron swarf released $\text{Fe}^{2+}$ throughout the reaction time and hence this method produced better results. In single dose addition, the active sites on iron surface might get occupied as the reaction progressed which reduced its catalytic action on persulfate oxidation and also reduced its involvement in Fenton like reaction.

The continuous presence of new active sites due to the sequential addition of iron particles effectively produced $\text{Fe}^{2+}$ ions that facilitated the degradation in a better way. The results were in accordance with Vicente et al (2011) and they reported that the incremental addition of iron enhanced the persulfate oxidation of Diuron compared to initial addition.

4.3.8 Effect of Temperature

The effect of temperature on oxidative degradation of pollutants was studied, in which sequential addition of 4 g/L (for textile effluent) and 3 g/L of iron-swarf (for pharmaceutical effluent) and mixing rate of 200 and 100 rpm respectively for DOX and US/DOX and initial pH of 3 were maintained.

The degradation was found to increase with an increase in bulk temperature during DOX process. In DOX, the COD reduction for textile
effluent was found to be 75, 84.09 and 95.45% at 30, 40 and 50°C respectively. At these temperatures, the COD reduction for pharmaceutical effluent was found to be 65.63, 78.13 and 93.75% respectively. The enhancement observed in DOX may be due to the fact that for most of the chemical reactions, increase in temperature will enhance the rate of reaction.

Similar to DOX process, in US/DOX also, the increase in temperature enhanced the COD removal. The complete degradation of textile effluent was achieved after 180 min at 30°C. At 40 and 50°C, complete degradation was obtained within 150 min. On the other hand, the complete COD removal for pharmaceutical effluent was achieved after 150 min at 30°C, whereas on increasing the temperature to 40 and 50°C, the time taken for complete COD removal was reduced to 120 and 90 min, respectively.

The results were contradictory to the results reported by Manousaki et al (2004) and Wang et al (2006). They observed that the rise in temperature inhibited the US degradation of organics. In contrast, recently Bel et al (2011) reported that the increase in temperature from 15 to 45°C nearly doubled (1.91 times) the sonolytic degradation of ciprofloxacin.

Consistent results have not been reported on the influence of temperature on sonolytic degradation of organics (Huang and Huang 2009). The change in temperature affects the gas solubility and surface tension (Wang et al 2006). Further the rise in temperature enhances the vapour pressure of solvent, which leads to less violent explosion of bubbles (Bel et al 2011). This produces much less temperature which severely affects the pyrolytic decomposition of organics and water molecules. Furthermore, the increase in temperature reduces not only the viscosity but also the dissolved gas content, which does not favor sonolytic degradation.
At the same time, increase in temperature enhances the number of cavitation bubbles and hence enhanced production of more oxidative radicals was facilitated. In addition, better mass transfer due to increase in temperature provides better reaction between oxidizing agents and pollutants. All these factors make the study on thermal effect on degradation as more complicated. Complexity still enhanced due to the use of real effluent which might contain hydrophobic and/or hydrophilic pollutants.

The bulk temperature dependency on reaction rate can be well described by Arrhenius equation (Equation 4.30), from which the apparent activation energy (E_a, J/mol), can be determined using reaction rates (k) observed at different temperatures (T),

\[
\ln k = - \frac{E_a}{RT} + \ln A \tag{4.30}
\]

where, A is the pre-exponential factor (1/min) and R is the universal gas constant.

The apparent activation energy for the degradation of pharmaceutical effluent was found to be 47.25 kJ/ mol for DOX process and 23.47 kJ/mol for US/DOX process. On the other hand, it was found to be 35.33 kJ/mol for DOX process and 20.6703 kJ/mol for US/DOX process for textile effluent.

It clearly showed that the catalytic action of ultrasound reduced the activation energy remarkably. Also, it can be observed that the activation energy required for degradation was found to be high for pharmaceutical effluent compared to that of textile effluent.

Huang and Huang (2009) studied the mineralization of phenol by UV/persulfate oxidation and reported the activation energy requirement as
25.99 kJ/mol. Recently Bel et al (2011) studied the effective removal of ciprofloxacin using sonolysis and reported that the activation energy required for the same as 17.5 kJ/mol. The required activation energy for the degradation of C.I. Reactive Red 2 using UV/US/TiO$_2$/Na$_2$S$_2$O$_8$ was reported as 9.26 kJ/mol (Wu 2009). The low value of activation energy observed in this study suggests the degradation is diffusion controlled as is the case for most radical reactions (Bel et al 2011).

4.3.9 Electrical Energy Consumption

The ‘Figure-of-merit’ electrical energy per order (EE/O) was found to be 1198 kWh/m$^3$/order for the ultrasound degradation of textile effluent. A tremendous reduction in energy requirement was observed when sonolysis was conducted along with aggressive oxidation caused by dual oxidant system, which was about 122 kWh/m$^3$/order.

Similarly the electrical energy consumption for the degradation of pharmaceutical effluent using sonolysis was found to be 2642 kWh/m$^3$/order. When the sonolysis was coupled with DOX system, the energy requirement was significantly reduced to 173 kWh/m$^3$/order. EE/O was not calculated for DOX system as no electricity was used during this process.

In order to overcome the energy crunch, industries across the world are taking stringent measures to curb the wastage of electricity. This study clearly shows that, ultrasound irradiation is not energy efficient when it was used alone for the destruction of pollutants. So sonolysis can be made attractive by coupling it with DOX system. In that way, coupling these two processes will minimize the energy requirement which is highly needed in the current scenario.
4.3.10 Biodegradability Analysis

The biodegradability of the wastewater was analyzed to study the performance of different methods investigated. The BOD₅/COD ratio of untreated textile effluent was 0.31. After sonication for 180 min, the ratio was found to be 0.45. The biodegradability of the effluent after treating with DOX system was found to be 0.54, while it was 0.69 after US/DOX treatment.

Similar study was extended to determine the biodegradability index of the pharmaceutical effluent before and after treatment processes. It was found that, the index of untreated pharmaceutical effluent was found to be 0.127, whereas it was nearly doubled after treatment using DOX process. When US/DOX was employed to treat pharmaceutical wastewater, the index was raised to 0.510.

This study clearly elucidates the capability of proposed treatment method viz., US/DOX on the enhancement of biodegradability which is highly required for better biodegradation. It also shows that with respect to pharmaceutical effluent, the enhancement was found to be insignificant as compared to textile effluent. This is attributed to the fact that some of the pollutants are recalcitrant towards the proposed treatment method and hence even after US/DOX, it is difficult to degrade the effluent through biological way.

4.3.11 Toxicity Test

The diameter of inhibition zone for the untreated textile effluent was found to be 19 mm while it was about 26 mm for untreated pharmaceutical effluent. After the degradation of effluents by proposed treatment methods,
the zone of inhibition was reduced to 8 mm for textile effluent whereas it was reduced to 13 mm for pharmaceutical effluent.

4.4 COMPARATIVE STUDY

In the present study, the industrial effluents such as textile and pharmaceutical effluents were treated using different hybrid treatment methods. The results obtained are presented in Table 4.3 and compared.

The results clearly show that, all the reported treatment methods produced better results for textile effluent in comparison with pharmaceutical effluent. Better enhancement in biodegradability index of textile effluent was achieved by using SFS compared to US/DOX, while for pharmaceutical effluent, US/DOX enhanced the index significantly compared to SFS.

The electrical energy consumption was found to be very less for the degradation of both the effluents using US/DOX, compared to SFS. The US/DOX treated textile effluent was found to be less toxic compared to that of SFS. For pharmaceutical effluent, SFS treated wastewater was less toxic compared to US/DOX.
Table 4.3  Comparison of the results obtained from different hybrid methods

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Textile effluent</th>
<th>Pharmaceutical effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Part-I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>% COD reduction by Sonolysis</td>
<td>39.13</td>
<td>20.31</td>
</tr>
<tr>
<td>% COD reduction by Fenton`s process at pH 3</td>
<td>27.27</td>
<td>14.06</td>
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<tr>
<td>% COD reduction by Fenton`s process at pH 5 (natural pH)</td>
<td>18.18</td>
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<td>% COD reduction by sorption process</td>
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<td>% COD reduction by sono-sorption</td>
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<td>% COD reduction by sono-Fenton process</td>
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<td>48.44</td>
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<tr>
<td>% COD reduction by sono-Fenton-sorption process</td>
<td>97.73</td>
<td>81.25</td>
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<td>Biodegradability index of untreated effluent</td>
<td>0.31</td>
<td>0.127</td>
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<td>Biodegradability index of effluent after SFS</td>
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<td>0.4</td>
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<td>Intra-particle diffusion coefficient, mg/(L.min)</td>
<td>Sorption:142.8</td>
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<td>SS :1696.0</td>
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<td></td>
<td>SFS :2304.0</td>
<td>SFS : 741.19</td>
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<td>Liquid film mass transfer coefficient, m³/min</td>
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<td></td>
<td>SS : 6x10⁻⁶</td>
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<td>SFS : 10x10⁻⁶</td>
<td>SFS : 8x10⁻⁶</td>
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<td>Limiting rate constant of reaction at maximum coverage under the given</td>
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<td>experimental conditions, min⁻¹</td>
<td>SFS : 2.56x10⁻²</td>
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<td>Equilibrium constant for adsorption of substrate on sorbent, L/mg.</td>
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<td>SS : 0.144x10⁻⁵</td>
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<td></td>
<td>SFS : 3.38x10⁻⁵</td>
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<td>Initial adsorption kinetic coefficient, L/(g.min)</td>
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<td>SS : 4.54x10⁻⁸</td>
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<td></td>
<td>SFS : 7.38x10⁻⁸</td>
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<td>Electrical energy consumption (kWh/m³/order)</td>
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<td>Sono-Fenton: 592.5</td>
<td>Sono-Fenton: 905</td>
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<td></td>
<td>SFS: 250.2</td>
<td>SFS: 358</td>
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<td>Pharmaceutical effluent</td>
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<tr>
<td>--------------------------------------------------------------------------</td>
<td>------------------</td>
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<td>20.31</td>
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<td>Electrical energy consumption (kWh/m³/order)</td>
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<td>US : 2642</td>
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<td>Untreated : 26</td>
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<td>After US/DOX: 08</td>
<td>After US/DOX: 13</td>
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