Ultrasound and Hydrogen Peroxide Assisted Organic Degradation of Petrochemical Wastewater

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Abstract: Irradiation with ultrasound (US) and hydrogen peroxide as advanced oxidation treatment techniques were carried out to treat a complex effluent (petrochemical wastewater). This technique has been used alone and the efficiency of these techniques was tested by comparing other conventional treatments. When used US exposure for 40 minutes yielded the best TSS, TDS, pH, alkalinity, and turbidity reduction. When used in combination of ultrasound and hydrogen peroxide. On the basis of the variation in the values of chemical and physical kinetic parameters it can be conducted that the type of treatment scheme affects the subsequent rate of the oxidation process.

Keywords: Advanced oxidation process, Hydrogen Peroxide, Organic matter, Petrochemical wastewater, Ultrasound.

1. Introduction: Petrochemical industries are most highly polluting industries with reference to water pollution. The quantity of wastewater generated from petrochemical industries is large and is characterized by a high pollution load. Benzene and chloride are most important raw materials used in the production of mono-chlorobenzene (by liquid phase chlorination of benzene process), large amount of a highly coloured spent wash remain in the process still and require disposal. The wastewater is characterized by a high concentration of dissolved solids, pH, TSS, turbidity, and acidity. Petrochemical wastewater contains all the organic and inorganic dissolved impurities present in the petroleum products. Due to high concentration of dissolve organic and inorganic matter, a host of treatment techniques have been proposed (Sheehan and Greenfield, 1980). Wet-air oxidation and anaerobic digestion are also employed; the latter being extensive used. Some method have been operated on an industrial scale, some of them pilot plant scale. Each of them of these techniques does have some technical or techno-economic problems. Hybrid method mentioned more than two oxidation processes which are used for wastewater treatment. The effect of ultrasound treatment using and hydrogen peroxide on the organic-degradation rate of the petrochemical industry has been discussed in this work.

Ultrasound is increasingly being seen as having potential for use in the treatment of the water, wastewater and sewage sludge. (Olson and Barbier, 1994) Sonochemical oxidation employs the use of ultrasound resulting in cavitation phenomena, which is defined as the phenomena of the formation, growth and subsequent collapse of micro-bubbles or cavities. It occurs in an extremely small interval of time (Milliseconds) releasing large magnitude of energy simultaneously at millions of such locations in water with contamination (A.H. Mahvi, 2009) Because of the highly localized concentrations of oxidizing species generated as a result of cavitations phenomena, such as hydroxyl radicals and hydrogen peroxide, (Stepniak Ionina et al, 2012;). The combination of the chemical and physical effects of cavitations, thus are responsible during the application of ultrasound in water and wastewater treatment. (Shah et al., 1999), ultrasound has been used in combination with technology such as ozone to improve water and effluent treatment ultrasound combination with ozone has been used to enhance the degradation of natural organic matter and cyclohexene.

From a variety of different sources have been reported to play an important role in various waste
treatment applications, in recognition of these potential advantages, recent research has focused on the development of sound based processes for the treatment of wastewater, solid wastes, hazardous waste, have summarized the ultrasound utilized in the field of wastewater treatment according to the categories of specific waste types, in our work, application of ultrasound as a treatment technology has been found to enhance the organic degradability of the effluent for the advanced oxidation process, this work investigates the feasibility of combining these techniques (ultrasound and hydrogen peroxide) in testing the petrochemical effluent.

2. Experimental:

2.1. Petrochemical wastewater

The petrochemical wastewater was procured from nearby Ujjain district (M.P.) India. And this was used for further study. Table 1 shows the characteristic of the petrochemical effluent.

Table 1 characteristic of effluent wastewater

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>10.1</td>
</tr>
<tr>
<td>2</td>
<td>BOD (mg/lit.)</td>
<td>81.1</td>
</tr>
<tr>
<td>3</td>
<td>COD (mg/lit.)</td>
<td>199.1</td>
</tr>
<tr>
<td>4</td>
<td>TDS (mg/lit.)</td>
<td>2030</td>
</tr>
<tr>
<td>5</td>
<td>Hardness</td>
<td>8.1</td>
</tr>
<tr>
<td>6</td>
<td>Turbidity (NTU)</td>
<td>91.1</td>
</tr>
<tr>
<td>8</td>
<td>Total Suspended solids</td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td>Chlorides</td>
<td>809.1</td>
</tr>
<tr>
<td>10</td>
<td>Alkalinity</td>
<td>8.1</td>
</tr>
</tbody>
</table>

2.1.2 Reactor

All the organic degradation studies were performed in a reactor made of glass having a capacity of 1 L. reactor is made by Borosil Company.

2.1.3 Magnetic stirrer

1 MLH magnetic stirrer manufactured by Remi equipments was used in the base of reactor, process was occurred at room temperature, and speed was low level.

2.1.4 Ultrasound setup- ultrasound device

In the present study, the cavitations experiments (Ultrasound treatment) were carried out using an ultrasound device. The setup used for this study is similar to.

2.2 Experimental protocol

2.2.1 Preparation of the effluent sample

The raw, effluent plant treated sample diluted 10 ml of $\text{H}_2\text{O}_2$ (hydrogen peroxide), and then this sample was ready for start experiment.

2.2.2 Ultrasound treatment

The experiments were carried out in an ultrasound setup. The volume of liquid was kept constant at 1.0 L. no pH adjustment was done during the ultrasound treatment step; the pH and other parameters was affected during the treatment. The effluent sample was subjected to ultrasound and magnetic stirrer for different time intervals. In this treatment effluent sample with ultrasound and hydrogen peroxide for 40 min. had shown encouraging results hence; lower and higher time intervals for same ultrasound (less than 40 min.) sonication periods of 30 min., 1 2 and 3 h were studied. One millilitre sample aliquots were withdrawn after every 10 min. of the treatment. A 10 minute break was given after every sampling during the US run to cool down the spent wash to the room temperature (Sangave P.C. et al., 2006), in this experiment the temperature was not investigated. Hence, the fall down in Total dissolve solids, pH, total suspended solids, turbidity and alkalinity. The effluent treated with ultrasound
then subjected to aerobic advanced oxidation to study its effect on the organic degradation.

2.3 Analysis:
All parameters which are mentioned in this paper were done according to standard methods of analysis of wastewater and water, (Pollution control board Ujjain, India).

3. Results and Discussion:
3.1 Effect of ultrasound treatment on the effluent
The effect of cavitations’ was studied as advanced oxidation process. Cavitations’ of the effluent was carried out at an operational ultrasound frequency of sweep frequency. The effect of this low frequency ultrasound for different exposure periods was studied in order to determine the optimum treatment conditions. The samples withdrawn were analyzed for the changes in TSS, TDS, pH, and chlorides. Within the range explored for the ultrasound exposure periods between 40 min. the effect of the ultrasound on the effluent, all the parameters are reduced. Fig showed the demonstrate role of ultrasound waves and the resultant cavitations in restructuring the molecules present in the waste. This observation holds true since higher ultrasound exposure period (1, 2, and 3 h) had very little effect on the net parameters changes of the effluent (Sangave P.C. et al., 2006).

A lot of studies have investigated the process feasibility with synthesis aqueous solutions containing model pollutants. In the case of a single compound, the concentration of the target pollutant and the first intermediate can be measured and their reaction kinetics can be modelled. But, in the case of a real wastewater system, ultrasound leads to the formation of multitudes of products due to the inherent complexity of the effluent, which in turn are difficult to identify (Gonze et al., 2003).

3.2 Effect of ultrasound on TSS (US + H$_2$O$_2$)
The TSS reduction of waste water as a function of the ultrasound reaction time for same doses each, mentioned in figure. The ultrasound dose kept constant for the same time intervals. Total suspended solids concentration is varies from 90 mg/l to 66 mg/l in the 40 minute applied ultrasound for petroleum effluent. We observed that TSS is gradually decreased with respect to ultrasound time. According to bureau of Indian standard and WHO guidelines and we achieved 99.1% in 40 minute of ultrasound irradiation by this process. (Lalwani P.et al., 2013 and national council for air and stream improvement, 2009)

![TSS Reduction graph](image)

**Fig.1 TSS Vs Ultrasound**
Fig. 2. TDS Vs Ultrasound

Fig. 3. pH Vs Ultrasound
3.3 Effect of ultrasound on TDS (US + H$_2$O$_2$)
The TDS reduction of petroleum industry wastewater as a function of ultrasound reaction time for various time zones, which mentioned in figure, the ultrasound dose kept constant. Since higher ultrasound exposure periods (1, 2, and 3h) also had very little effect on the net TDS and COD change of the effluent. (Sangave P.C.et al., 2004), because of low frequency ultrasound very powerful in hydro–Mechanical shear forces are in bulk liquid surrounding the bubble. The mechanical Forces are more effective at frequency below 100 kHz. (Tiehm and Neis, 2004). Concentration of total dissolve solid is decrease with respect to ultrasound applying for 0 to 40 minutes on the petrochemical effluent. We are seeing in the fig. 2, the TDS concentration gradually decreasing from 1998 mg/l to 1965mg/l. According to WHO, TDS Reduction achieved 99.3%.

3.4 Effect of ultrasound on pH (US + H2O2)
The pH reduction of waste water as a function of the ultrasound reaction time for same doses each, mentioned in fig. 3, the ultrasound dose kept constant for the same time intervals. Fig.3 demonstrates the removal of aromatic contamination (Monochlorobenzene) by the Sonochemical process at different pH. It is clearly seen that lower pH values favored the organic degradation. (Maleki A. et al., 2007). According to Fig. 3, the pH ranges varies from 8.2 to 6.5 and as per the WHO guidelines desirable limit is 6.5- 8.5 and we achieved that limit, and pH concentration reduction is 99.1% observed.

3.5 Effect of ultrasound on chlorides (US + H2O2)
The chloride reduction of waste water as a function of the ultrasound reaction time for same doses each, mentioned in fig. 4, the ultrasound dose kept constant for the same time intervals. According to fig. 4., removal of chlorides contamination by the ultrasound process at 40 min. of time period. It was observed that chlorides are reduced from the range of 799.7 mg/l to 766.4 mg/l. The total reduction of chlorides is 98.2 % from the effluent. (Basu, K. Manas et al. 2000).

4. Conclusion:
The effect of acoustic cavitations (US treatment) and hydrogen peroxide in the treatment of raw petrochemical wastewater have been investigated. From the experiments, it has been established that the low intensity ultrasound (radical formation and shear forces) brings about transformations of the effluent constituent at a molecule level. Rather than the Sonochemical effects of the ultrasound, the powerful hydrodynamic shear forces governed these transformations. Hence the acoustic cavitations generate good results. The combination of the ultrasound and hydrogen peroxide yielded the best TSS, TDS, pH, and Chlorides, removal efficiency as compared to the processes when they were used as stand- alone treatment techniques.

References:


