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Treatment of laundry wastewater by UVC-based advanced oxidation process – A case study

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The main aim of this research is to evaluate the treatment of laundry wastewater by the UV-H_2O_2 advanced oxidation process. The COD and BOD of the wastewater were about 800 mg/L and 120 mg/L respectively, which indicate that the wastewater is poorly biodegradable. In batch operation with simultaneous exposure to 8 UV lamps, H_2O_2 doses were 10, 20, 30 and 40 mg/L. The percentage removal of COD was 42%, 53%, 77% and 75% respectively. The biodegradability index increased with increase in peroxide dose. The degradation followed first order kinetics and the kinetic constants were 0.0045, 0.0059, 0.0117 and 0.0119 min^{-1} for peroxide dose of 10, 20, 30 and 40 mg/L respectively. In continuous mode operations with longer exposure but to one UV lamp at a time, the COD removal efficiency was 25%, 43%, 45%, 48%, 57% and 32% respectively for peroxide doses of 5, 10, 20, 30, 40 and 50 mg/L respectively.

Keywords: Laundry, surfactant, advanced oxidation process, AOP, UV/H_2O_2, UVC.

Introduction

During the past few decades, uncontrolled rise in contaminant disposal into water bodies has led to enhanced pollution levels. The main causes for this have been industrial development, population explosion and rapid development of urban areas[1]. Post industrialization, wastewater from industrial activities has been found to have a large concentration of recalcitrant organics, and they inevitably increase the level of pollution of natural water bodies. One such recalcitrant organic is surfactant, which is the main component of maximum number of detergents used in the laundry industry[2]. When discharged into water bodies, they inhibit the growth of algae and other microorganisms and reduce the productivity of the water. High concentration of surfactants can be toxic to fishes, as they absorb them through their gills and then they are carried to the entire body by blood circulation. Apart from this, when the concentration of surfactants in water bodies exceeds 0.1 mg/L, persistent foam appears on the surface and there is a drastic fall in the concentration of dissolved oxygen of water[3]. It is therefore essential to treat the laundry wastewater, before it can be safely disposed into water bodies.

In the present study, laundry wastewater was considered as it contains considerable amount surfactants which are one of the major forms of recalcitrant organics. Also, the biodegradability of laundry wastewater is extremely low and conventional treatment techniques, including biological processes are not suitable for remediation of such wastewater. This necessitated the need to attempt to treat the wastewater by advanced process. It has been observed that the conventional approaches to the treatment of such pollutants often prove insufficient to meet the regulations laid down in view of rising water pollution[4]. This has led to the requirement of new and more efficient methods of wastewater treatment, leading to the development of chemical oxidation techniques such as mineralization, which breaks down organics to CO_2 and H_2O or at least converts pollutants to less toxic compounds. One such prominent technique is the advanced oxidation process (AOP), some examples of which are O_3/H_2O_2 process[5], UV photolysis, Fenton process, photo-Fenton process and UV-H_2O_2 process[6]. Among these AOPs, UV-H_2O_2 process has many advantages compared to others. In this process, the rate of organic decomposition increases with increase in H_2O_2 dose up to an optimum limit. Beyond this, the process efficiency reduces with increase in dose. The main principle behind this process is that when the oxidants are exposed to UV radiation, the energy of radiations disintegrates the oxidants leading to the formation of hydroxyl radical, by the photolysis of H_2O_2[7]. The hydroxyl radical can non-selective degrade the organic compounds. The process has been found to be suitable and efficient for removal of chemical oxygen demand (COD) from olive mill wastewater[8].

The objective of this study was to assess the treatment of laundry wastewater by UV-H_2O_2-based AOP by batch and continuous mode operation. The particular aims of this work were to evaluate the efficiency of treatment in both systems, to obtain the conditions corresponding to optimum treatment. The other aim was to evaluate the effect of this treatment on the biodegradability of the wastewater. The holistic target of the work was to obtain optimum removal so that any further treatment, if necessary, can be carried out by biological operations.

Materials and methods

The main chemical compound used for this project was hydrogen peroxide (H_2O_2), having a stock solution strength of 30% by volume. The corresponding strength in terms of mass/volume was found to be 6.709 g/L. The pH of the raw sample has been maintained at 7–8 using 30% hydrochloric acid by diluting the same to10%.

Wastewater was collected from laundry industry situated at Santragachi, West Bengal. The physicochemical characterization of the wastewater was carried out as per the standard method for water and wastewater examination. The wastewater was neutralized to reduce the pH in the range of 7–8 by dilute hydrochloric acid and used for the further experiments.

For continuous mode operation, the experimental setup is depicted in Fig. 1. It consists of three UV cartridges arranged in series, such that the outlet of one is connected to the inlet. Each cartridge is fixed to rounded wooden rods and the entire framework is clamped to a wooden base. Each cartridge has provision to hold one UV lamp. Of the three cartridges, two are connected to a power source which means that effectively, two lamps have been used during the experimental process. Up-flow condition has been maintained along with a constant flow rate of 1 mL/min by means of a peristaltic pump. The hydrogen peroxide doses were 5, 10, 20, 30, 40 and 50 mg/L.

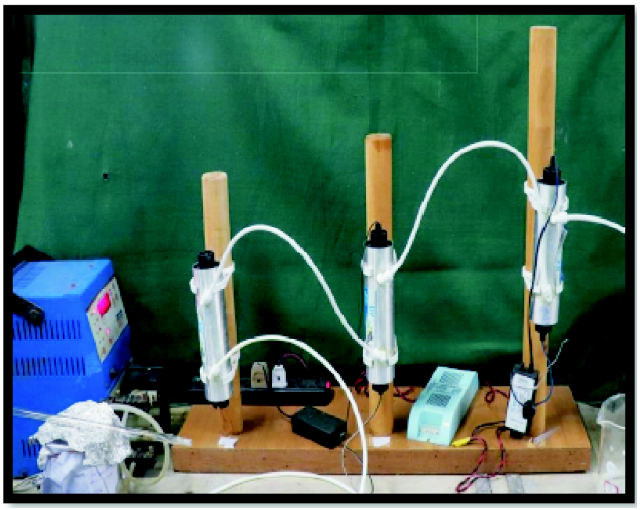

Fig. 1. UV cartridges for AOP reactor in series arrangement.

The batch reactor (Fig. 2; Make: M/s. Lab Tree) used for carrying out batch mode treatment of wastewater consists of eight UV lamps, fitted inside a metal box having a polished stainless-steel enclosure. 100 mL of wastewater sample having prerequisite dose of hydrogen peroxide (0, 10, 20, 30 and 40 mg/L) was irradiated and samples were withdrawn at certain interval for determination of remaining COD and biochemical oxygen demand (BOD). Assuming first order kinetic

Fig. 2. AOP batch reactor.

model for batch mode operation, the rate of reaction can be expressed in the following form[9]:

$$\ln \frac{[C]}{[C]_0} = -k'_{app}\, t \quad (1)$$

In the above equations, C_0 = initial concentration of organics (at t = 0), C = concentration at any time t and k = reaction rate constant. From the slope of the plot of $\ln\frac{[C]}{[C]_0}$ vs t the rate constant can be determined.

Results and discussion

The laundry wastewater was analyzed for its physico-chemical characterization after its collection. The important parameters are given in Table 1. It is important to note that the pH of raw wastewater was considerably high. In order to have efficient performance of the system, it is imperative that the pH be reduced to 7–8, and the same was achieved by the use of 10% of 30% hydrochloric acid. The solid concentration in the wastewater was found to be very high; though the suspended solid concentration was quite low. Thus, the turbidity of the wastewater was in the range of 10–30 NTU. The most important inference from characterization tests was that the biodegradability index (ratio of BOD and COD) of the wastewater was very low indicating the wastewater is not suitable for biological treatment.

When treatment was carried out under batch operation, high COD removal was observed within two hours. In the four batch operations carried out at H_2O_2 doses of 10, 20, 30 and 40 mg/L for a period of 2 h in each trial, the corresponding COD removal efficiency obtained after two hours of UV exposure was 42%, 53%, 77% and 75% (Fig. 3). It is to mention that no COD removal was achieved under UV for a period of 2 h, in absence of H_2O_2 dose. The first order rate constants were found to be 0.0045, 0.0059, 0.0117 and 0.0119 min^{-1} respectively for 10, 20, 30 and 40 mg/L peroxide doses respectively (Table 2). The biodegradability index of the effluent was found to increase with increase in H_2O_2 dose. These values were 0.31, 0.37, 0.64 and 0.74 for 10, 20, 30 and 40 mg/L peroxide doses respectively. This result demonstrates that transformation products were more biodegradable compared to the parent products. The effluent can be effectively treated by biological processes.

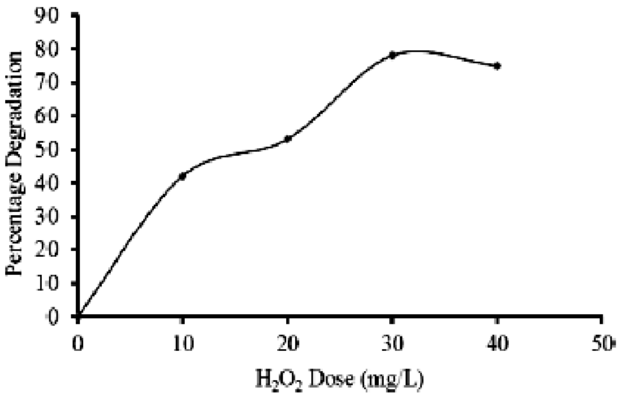

Fig. 3. Effect of H_2O_2 dose on COD removal efficiency in batch system.

Table 1. Wastewater characteristics

Properties	Value
pH	9.5–11.5
Turbidity (NTU)	10–30
UV_{254} absorbance (cm^{-1})	0.7–0.8
Total alkalinity (mg/L) as $CaCO_3$	400–600
Total hardness (mg/L) as $CaCO_3$	300–400
Chlorides (mg/L)	400–600
Total solids (mg/L)	3,300
Dissolved solids (mg/L)	3,150
Suspended solids (mg/L)	150
COD (mg/L)	800
BOD (mg/L)	120
BOD/COD	0.10–0.15

Table 2. Effect of H_2O_2 dose on kinetic constant

H_2O_2 dose (mg/L)	Kinetic constant (min^{-1})	R^2
10	0.0045±0.0006	0.987
20	0.0058±0.0009	0.987
30	0.0117±0.0013	0.994
40	0.0119±0.0029	0.983

In continuous mode operation, it was observed that maximum COD removal occurred within the first four hours and steady state condition was achieved thereafter for all trials. As observed from Fig. 5, with varying H_2O_2 doses of 5, 10, 20, 30, 40 and 50 mg/L, the 24 h COD removal percentage was observed as 25%, 43%, 45%, 48%, 57% and 32% re-

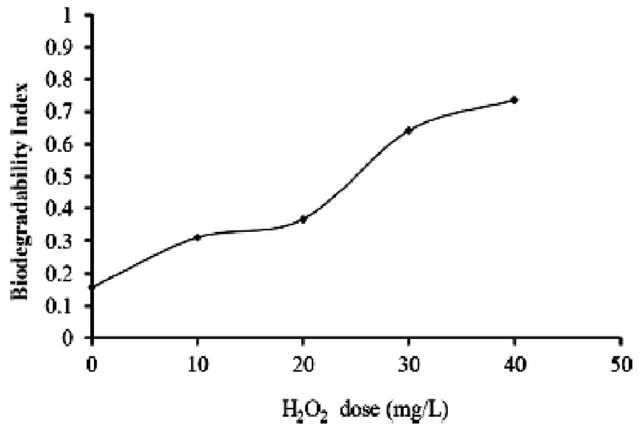

Fig. 4. Effect of H_2O_2 on effluent biodegradability in batch system.

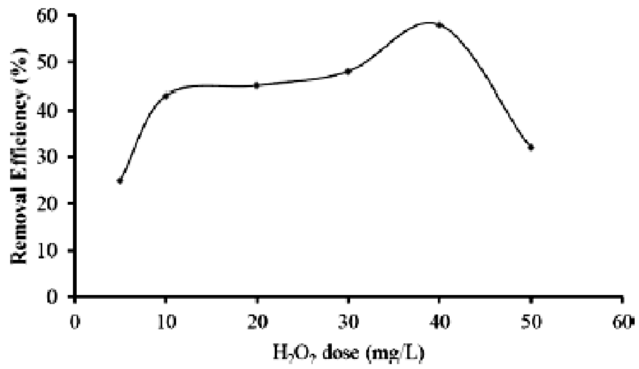

Fig. 5. Effect of H_2O_2 dose on COD removal efficiency in continuous system.

spectively and the biodegradability index increased from initial conditions of 0.10–0.15 to 0.25, 0.56, 0.60, 0.88, 0.59 and 0.24 respectively (Fig. 6).

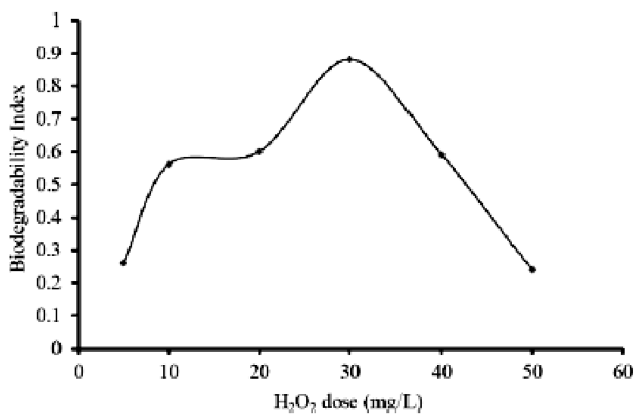

Fig. 6. Effect of H_2O_2 dose on effluent biodegradability in continuous system.

Maximum removal is observed at a H_2O_2 dose of 40 mg/L, where 57% degradation occurred after a period of 24 h. The efficiency of the process then reduced to 32% at a higher dose of 50 mg/L. This is because beyond the optimum concentration, the H_2O_2 decomposes to H_2O and O_2. This leads to recombination of hydroxyl radicals and they are not available as free radicals for attacking organic substrates present in the wastewater[10]. This means that excess peroxide concentration acts as scavenger of the free radicals, which is the phenomenon of H_2O_2 scavenging on hydroxyl radicals[10]. This phenomenon is illustrated by the two following equations, which are the two ways of recombination or scavenging of hydroxyl radicals by hydrogen peroxide itself:

$$HO^{\bullet} + HO^{2\bullet} = H_2O + O_2 \quad (2)$$

$$HO^{\bullet} + HO^{\bullet} = H_2O_2 \quad (3)$$

Also, it is observed from Fig. 6 that the effluent biodegradability index also increased to an optimum of 30 mg/L and then subsequently reduced. The biodegradability of treated wastewater was highest at 40 mg/L for batch and 30 mg/L for continuous operation. This difference is due to the fact that removal efficiency is assessed in terms of COD, while biodegradability index also requires the assessment of BOD and the change in the two parameters is not same for different doses. This demonstrates the reason for difference in optimum dose for removal efficiency and biodegradability index, because biodegradability index depends on the increase in BOD along with decrease in COD of the wastewater, while removal efficiency is assessed only in terms of decrease in COD. In case of batch operations, at 30 mg/L, the final BOD has increased to 114 mg/L while COD has reduced to 178 mg/L and at 40 mg/L, COD is 197 mg/L and BOD is 145 mg/L. In continuous operations, the final COD and BOD at 30 mg/L are 395 mg/L and 348 mg/L respectively and at 40 mg/L, they are 441 and 263 mg/L respectively.

Conclusions

The initial characterization of wastewater from laundry industry showed that the biodegradability index of the raw wastewater was quite low and the pH was quite high. The pH was brought down to a considerable level before UV-H_2O_2 treatment. The maximum removal of COD by UV-H_2O_2 process was found to be was 78% at 30 mg/L for batch and 58% at 40 mg/L for continuous mode operations. Beyond this point, a reduction in removal efficiency is observed. The removal of COD followed the first order reaction rate and the kinetic constants were evaluated. The efficiency of the process depends on the rate of generation of hydroxyl radicals and period of contact between the radicals and the organic. The rate of generation was higher in batch system due to the simultaneous exposure of eight UV lamps when compared to only one exposure at one point of time. Although the period of contact was higher in the continuous system, the rate of generation prevailed over the period of exposure in determining the efficiency of the two systems. In batch system, final COD was found to be than the limit of 200 mg/L as per IS 2490 (1983)[11] for Tolerance Limits for Industrial Effluents. Since the biodegradability of the wastewater was found to increase considerably, this UV-H_2O_2 process can be used as a pre-treatment before biological process.

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