Treatment of Real Tannery Wastewater by Nanocavitation Based Hybrid Oxidation Methods

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Abstract— Tannery sector is a main contributor for the development of Indian economy, exports and also provides large scale employment.This industry produces a substantial quantity of highly complex toxic effluents which can cause severe water pollution. Presence of recalcitrant organic pollutants in the tannery effluent create a major problem for efficient treatment of real tannery wastewater.These organic pollutants cannot be completely oxidized by the usual physiochemical and biological methods because of its complex nature.This study focuses on the removal of organic pollutants present in tannery wastewater by Hydrodynamic cavitation(HC) reactor and its combination with other oxidizing agents like HC+ozone,HC+ozone+hydrogen peroxide(H2O2) and HC+Ozone+Fenton reagents.The effect of different types of parameters like inlet pressure,initial concentration of tannery effluent, ,concentration of ozone, hydrogen peroxide (H2O2) and Fenton reagent on pH,COD,,TOC,TDS,TSS on the tannery wastewater were studied.The experiment consist of two different procedures by varying these operating parameters. In the first procedure, wastewater was subjected to cavitation alone and in the second procedure wastewater was subjected to cavitation based hybrid oxidation technique with the purpose of maximizing the extent of mineralisation.The novel integration of hydrodynamic cavitation with oxidizing agents results in 80-85% removal of COD and TOC under optimized conditions.

Index Terms—Advanced Oxidation Process,Hydrodynamic cavitation,Hydrogen Peroxide,Fentons reagent,Ozonation,Recalcitrant Pollutants, Real Tannery wastewater

1 INTRODUCTION

Tanning is one of the oldest technology of converting skin and hides of animals into leather. s. Leather industries produce highly polluting wastewater as they consume approximately 300 kg of chemicals (lime, salt, chromium, tannin acids etc.,) and 34 to 56 m3 of water per ton of raw hide [2,3] when processed according to the conventional methods. Tannery waste effluents (TWE) are characterized by their high chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC), variation in pH, solid contents, conductivity, and turbidity [4-7].High concentration of refractory organic waste present in tannery wastewater makes it difficult to be treated by conventional methods like ion exchange ,adsorption, chemical coagulation, flocculation and activated sludge process .(7-11)Due to the limitations of the above chemical and biological treatment processes, alternative treatment technologies are necessary to be developed for the treatment of tannery effluent.

In recent years, cavitation as an advanced oxidation process (AOP) has been receiving greater attention for the treatment of wastewater [12-14]. Cavitation comprises of the nucleation, growth, and subsequent collapse of micro-bubbles or cavities, occurring in a small time interval at multiple locations in the reactor and thus releases large magnitude of energy [13]. The collapse of cavities creates the 'hot spots' (a very high temperature and pressure region) resulting in the formation of •OH, •H, HO_2• and also H_2O_2 [16-17]. In the last two decades, ultrasonication has been studied for wastewater treatment [18-20], however it has not found any application so far on an industrial scale due to the higher maintenance costs involved and lower energy efficiency [13].

An alternative cavitation technology i.e. HC has been found to be more energy efficient as compared to acoustic cavitation for the degradation of organic pollutants and which can also be operated in a continuous mode [12,15, 21-24]. The degradation efficiency of HC can be improved by combining with other advanced oxidation processes/oxidizing agents such as H2O2, Fenton's reagent, ozone and photocatalytic oxidation [13-14, 22, 25-27]. Mishra and Gogate [25] investigated the degradation of Rhodamine B dye using HC in the presence of intensifying additives. They found that almost 59.3% degradation and 30% TOC reduction were achieved using HC alone at an optimized inlet pressure of 4.84 atm and solution pH of 2.5. The degradation efficiency was further increased to 99.9% along with 55% reduction in TOC when HC was combined with hydrogen peroxide (200 mg/L). Gogate and Bhosale [26] studied the combined approach for the degradation of Orange Acid II dye and reported that combination of HC with oxidizing agents such as sodium persulfate, H2O2 and NaOCl was found to be better as compared to use of the individual oxidants. Almost complete degradation of Orange Acid II was obtained in 60 min using HC in combination with sodium persulfate (535.72 mg/L) oxidant.

Although many studies report on the degradation of synthetically prepared tannery wastewater using HC coupled with various oxidative additives mostly at low concentration ranges (i.e. 50 -100ppm), however smaller number of study has been reported so far for real tannery waste effluent. It is necessary to study the efficacy of HC and its hybrid processes for treating real Tannery waste effluent before applying on an industrial scale. This study focuses on investigating the performance of HC system for treating the Tannery effluent. Effects of process parameters (operating inlet pressure and dilution) on the TOC, COD ,TDS,TSS were investigated. In order to enhance the efficiency of HC, the effect of advanced oxidative reagents such as hydrogen peroxide, ozone, and Fenton in

combination with HC were also studied.

2 MATERIAL AND METHODS

2.1.Hydrodynamic Cavitation Reactor setup

Schematic representation of HC reactor set-up used in the present study is shown in Fig. 1. HC reactor set-up comprises of a closed loop circuit with a storage tank (25 L), manual valves, pressure gauges, a flow meter, and a high-pressure piston pump (power rating 2.2 kW). Pipes used in the HC reactor have an internal diameter of 19 mm. The bottom of the storage tank was connected to the suction side of the pump. The discharge from the pump was distributed into two lines: main line and bypass line. The main line consists of a cavitating device (slit venturi) and the flow rate in the main line was maintained by regulating the speed of the motor through variable frequency drive (VFD). The dimensions of the slit venturi used in this study are given in Table 2. Studies already reported by Rajoriya et al. [30] on the same HC reactor and slit venturi have identified the optimized cavitation conditions such as inlet pressure and cavitation number for obtaining the highest cavitational intensity, which was used as basis for performing the cavitation phenomena in our experimental studies.

2.2 Tannery Waste Effluent(TWE)

The tannery wastewater was collected from a leather processing company at Erode,Tamilnadu. (sources are not given due to the confidentiality issues). Samples were stored in a deep freezer and allowed to achieve room temperature before conducting experiments.

TABLE 1

CHARACTERISTICS OF TANNERY WASTE EFFLUENT

Parameter	Range	Unit
pH	7.2-7.5	-
COD	8800-10080	mg/L
TOC	2290-2500	mg/L
TDS	18000-20000	mg/L
TSS	17000-19500	mg/L
BOD	2800-3200	mg/L
Chromium	Not detectable	mg/L

2.3 Chemicals

For chemical oxidation of tannery wastewater the following chemicals such as hydrogen peroxide (30% w/w), ferric sulphate heptahydrate ($FeSO_4.7H_2O$) was procured from Karnataka Fine Chemicals,Bangalore, India .Sodium hydroxide pellets(NaOH) and 98%sulphuric acid (H_2SO_4) were procured from S. D. Fine Chemicals Ltd., Mumbai, India for adjusting acidic and basic pH condition of the tannery wastewater. All the chemicals were used as

received from the supplier. Wastewater was supplied by the local tannery industry and its original characteristics are shown in Table.1. TOC-LCPN analyser (TOC-LCPN analyser, Shimadzu, Japan) was used for determining the suspended total organic carbon (TOC) in the wastewater samples.

2.4 Analytical Procedure

A pH meter (Thermo scientific, USA) was used to determine the pH of the solution throughout the experiments. Total organic carbon (TOC) content of tannery effluents was measured using TOC analyzer (GE InnovOx). Biological oxygen demand (BOD) and chemical oxygen demand (COD) of samples were determined as per the standard APHA methods [31]. The conductivity and total dissolved solids (TDS) were measured using ion meter (Thermo scientific, USA). Total suspended solids (TSS) was determined by subjecting the TWE samples to filtration and drying whereas the total solids (TS) of the samples were determined by direct drying, both at 104°C in an oven (Make: DAIHAN Scientific Co. Ltd.) as per APHA methods. Turbidity was measured using turbidity meter (Spectra lab NT-4000). All experiments were repeated twice and reported

3 TREATMENT METHODOLOGY

Tannery samples of constant volume were initially subjected to HC treatment alone in the HC reactor in order to identify the optimum operational characteristics with respect to the inlet pressure and corresponding cavitation number.25L of the tannery sample volume was treated by recirculation in the closed circuit for 120min and process temperature was also maintained constant at 30±2C. The inlet pressure at the venture was varied in the range of 300-1000kPa and studied for obtaining operational cavitation conditions such as flow rate, fluid velocity and cavitation number.TWE samples were drawn at regular intervals of 30minand analyzed for changes in its COD and TOC which are indicative of degradation. The reaction mechanism for the dissociation of water molecules into the hydroxyl radicals and subsequent mineralization of the organic pollutants present in TWE by the hydroxyl radicals during the cavitation process . The TWE samples had high TDS,TSS and organic matter content and therefore dilution of the samples may affect the degradation rate. Therefore, the effect of dilution was studied by diluting the TWE samples in different proportions 25% and 50%(v/v) using double distilled water and was further subjected to HC at the optimized pressure conditions obtained from pressure study. In order to enhance the treatment efficiency,.the HC process was operated in combination with various oxidizing agents such as O3,H2O2 and Fentons reagent has
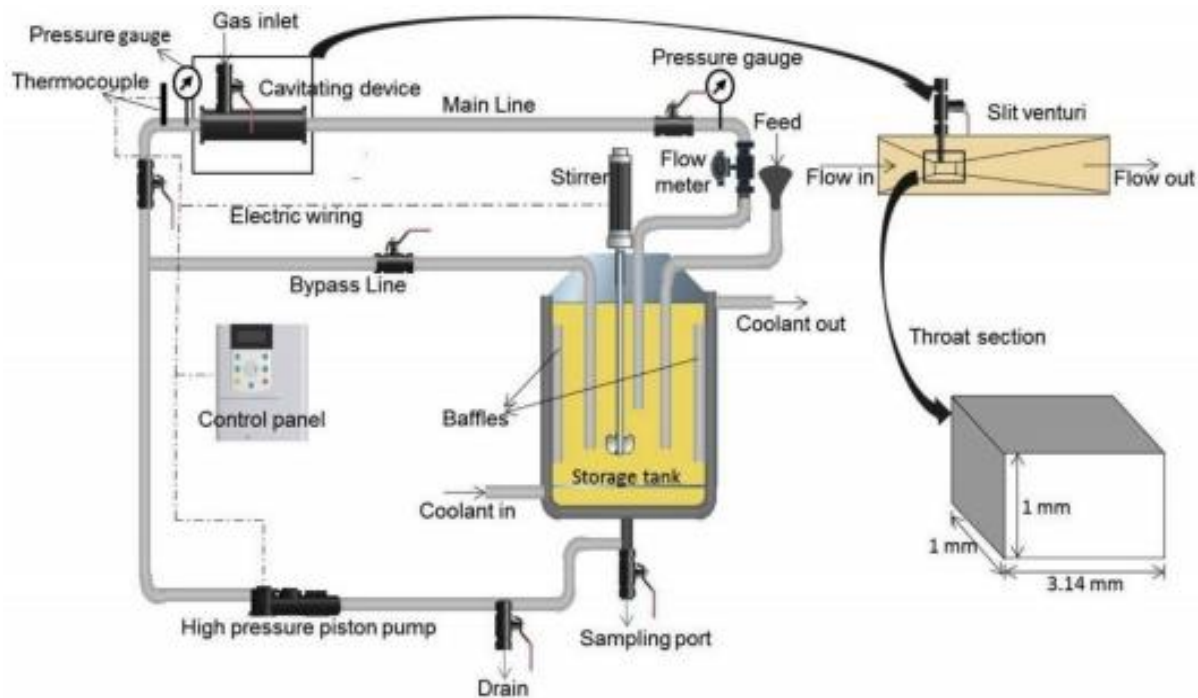
FIG. 1. SCHEMATIC REPRESENTATION OF HC REACTOR SETUP

various limitations such as high mass transfer resistances,slow rate of mineralization etc., which can be overcome by utilizing hybrid processes such as HC in combination with these advanced techniques. O3 required for the treatment was generated using O3 generator(High voltage corona discharge ozonator,maximum O3 rate:10g/h,make :Eltech Engineers,India)which was introduced at the throat section of the cavitating device through a nozzle.Effect of varying feed rate of O3 ,H2O2 and Fenton reagent were studied.

4.RESULTS AND DISCUSSION

4.1. Effect of inlet pressure and cavitation number on HC reactor performance

The extent of degradation of the organic pollutants in the water medium depends on the cavitational intensity which in turn depends on the operating inlet pressure, fluid flow rate or velocity through the venturi, and therefore these parameters were initially established to maximize the efficacy of HC. The other parameter which collectively represents the effect of pressure and fluid velocity through the venturi is the cavitation number (Cv). Cavitation number quantifies the cavitational intensity of a cavitating device(Rajoriya et al., 2016) and is defined as the ratio of the pressure drop between the throat and extreme downstream section to the kinetic head at the throat.. The cavities are generated under the ideal condition i.e. at Cv≤ 1, but in many cases, cavities can get generated at Cv > 1 due to the

existence of little dissolved gases and suspended particles (Saharan et al., 2013). A rectangular slit venturi having a flow area of 3.14mm2 was used as the cavitating device and the inlet fluid pressure was varied in the range of 300-1000 kPa. Table 2 provides the data of inlet pressure with their corresponding flow rate, velocity at the throat section, cavitation number and percentage reduction of TDS, TSS, COD, BOD and TOC for 120 min cavitation of the TWE sample.It has been observed that as the pressure increases from 300 to1000 kPa, the fluid velocity increases from 45.86 to 61.48 m/s whereas the cavitation number decreases from 0.092 to 0.051. Fig. 2 presents the effect of inlet pressure on the reduction in COD and TOC of the TWE with respect to the HC treatment time. The % reduction in COD and TOC increased with increase in pressure from 300 to 500 kPa and achieving a steady state in 120 min. It may be attributed to the fact that more cavities were generated as the pressure increased and thereby producing higher cavitational yield. However, with further increase in pressure from 500 to 1000 kPa, the % COD and TOC reduction decreased. As the inlet pressure exceeded the optimum pressure, choked cavitation, which is a condition of partial cavity collapse or inactive cavity collapse took place which reduced the cavitational intensity and led to a decrease in the extent of formation of free radicals (Saharan et al., 2014).

Therefore, the optimum inlet pressure of 500 kPa was found to be most suitable for all further treatment of TWE in the HC reactor.Table 2 presents that there has been

TABLE 2

HC CHARACTERISTICS AND EFFECT OF HC INLET PRESSURE ON PH, COD, TOC, TDS, TSS, BOD AND BI OF TWE.

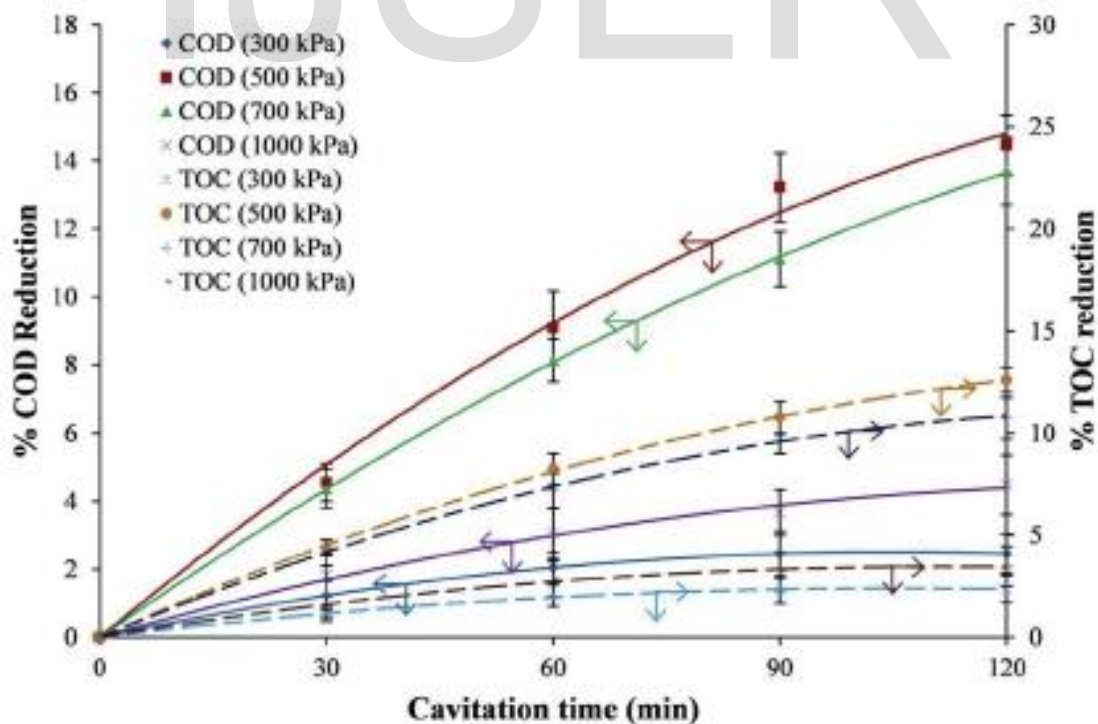| Parameters		HC inlet pressure			
		300 kPa	500 kPa	700 kPa	1000 kPa
Flow rate (m^3/s)		1.4×10^{-4}	1.6×10^{-4}	1.7×10^{-4}	1.9×10^{-4}
Velocity (m/s)		45.86	52.55	55.74	61.48
Cavitation number (C_v)		0.092	0.070	0.062	0.051
pH	Initial	7.27	7.35	7.36	7.43
	Final	7.31	7.54	7.44	7.56
COD (mg/L)	Initial	9760	9680	10080	9820
	% reduction	2.45	14.46	13.69	4.48
	Rate constant (min^{-1})	0.0003	0.0016	0.0014	0.0005
	R^2	0.94	0.99	0.99	0.94
TOC (mg/L)	Initial	2365	2349	2583	2477
	% reduction	2.36	12.60	10.72	3.47
	Rate constant (min^{-1})	0.0003	0.0013	0.0012	0.0004
	R^2	0.92	0.99	0.99	0.93
TDS (mg/L)	Initial	19680	20370	19640	19120
	% reduction	2.38	10.01	5.90	4.60
TSS (mg/L)	Initial	18680	18950	19800	18740
	% reduction	12.9	34.82	24.74	22.03
COD/TOC	Initial	4.12	4.12	3.90	3.96
	Final	4.12	4.03	3.77	3.92
BOD (mg/L)	Initial	–	3200	–	–
	Final	–	3600	–	–
BI	Initial	–	0.33	–	–
	Final	–	0.43	–	–

Fig. 2. Effect of operating inlet pressure on COD and TOC reduction (Experimental conditions: sample volume, 7 L).

an increase in the sample pH after HC treatment which is due to the generation of the hydroxyl radicals. It was observed from Table 2, that maximum COD and TOC reduction of 14.46% and 12.60% respectively was obtained at 500 kPa optimum pressure within 120 min. The reduction in TDS and TSS were also observed to be maximum at 10.01% and 34.82% at 500 kPa Pa inlet pressure. Moreover, the BOD value increased from 3200 to 3600 mg/L and the BI value changed from 0.33 to 0.43. This indicates that biodegradability of the sample has increased as the more recalcitrant organic molecules have been broken down into biologically degradable compounds. The COD to TOC ratios remained constant around 3.9 to 4.1 for all the TWE samples before and after cavitation at all pressures. This indicates that the reduction in COD corresponds to the reduction in TOC simultaneously. The TWE degradation rate kinetics depends on the hydroxylation of TWE by the OH radicals produced during HC or by its thermal decomposition within the cavitation bubble or at the bubble liquid interfacial region. The

Table 3
Effect of dilution on pH, COD, TOC, TDS, TSS, BOD and BI of TWE.

Parameters		HC + Dilution		
		No dilution	25% dilution	50% dilution
pH	Initial	7.35	6.89	6.66
	Final	7.54	6.95	6.98
COD (mg/L)	Initial	9680	8360	5520
	% reduction	14.46	15.31	18.84
	Quantum of reduction	1400	1280	1040
	Rate constant (min^{-1})	0.0016	0.0017	0.0023
	R^2	0.999	0.948	0.970
TOC (mg/L)	Initial	2349	2131	1627
	% reduction	12.60	12.76	17.33
	Quantum of reduction	296	272	282
	Rate constant (min^{-1})	0.0013	0.0015	0.0020
	R^2	0.986	0.973	0.974
TDS (mg/L)	Initial	20370	14770	10620
	% reduction	10.01	3.52	3.67
TSS (mg/L)	Initial	18950	13830	9800
	% reduction	34.82	34.92	42.85
COD/TOC	Initial	4.12	3.92	3.39
	Final	4.03	3.81	3.33
BOD (mg/L)	Initial	3200	–	1400
	Final	3600	–	1600
BI	Initial	0.33	–	0.25
	Final	0.43	–	0.35

intense micro mixing during the implosion of the cavities and microstreaming of fluid jets in the liquid medium increase the interaction of the hydroxyl radicals with the pollutant molecules, are resulting in better utilization of the radicals for the degradation.Incase of wastewaters with high organic and inorganic load present in the form of dissolved and suspended matter, dilution of the samples

50% dilution of the TWE sample. However, from Table 3, it can also be observed that as the degree of dilution increased, the quantum of COD reduction was reduced by 26%, whereas the quantum of TOC reduction was reduced by 5%, which indicates that there is no

pseudo first order kinetic expression fitted well for COD and TOC degradation rate kinetics data at varying pressure conditions and Table 2 presents the corresponding rate constants. It was observed that the rate constant of COD and TOC reduction increased from 0.3 × 10-3 to 1.6 × 10-3 min-1 and from 0.3 × 10-3 to 1.3 × 10-3 min-1 with increase in pressure from 300 to 500 kPa respectively. Further as the pressure increased from 500 to 1000 kPa, the rate constant of COD and TOC reduction decreased to 0.5× 10^3 and 0.4×10^3 respectively. Similar results have been reported by Rajoriya et al. (2018), for the treatment of textile dyeing industrial effluent using HC wherein they have reported that maximum of 17% TOC and 12% COD reduction was obtained at an optimum inlet pressure of 500 kPa.

4.2. Effect of dilution on efficacy of HC

Under the cavitational conditions created in the HC reactor, the highly reactive hydroxyl radicals which are formed have a redox potential of 2.80 eV and target any kind of pollutant nonspecifically and mineralize them completely. Moreover, the conditions of microturbulence, may alter the concentration of the hydroxyl radicals generated as well as the probability of its interaction with the pollutant molecules in the cavitational reactors, thereby affecting the overall degradation rate. Therefore, in order to understand the effect of dilution as well as effect of initial concentrations of TWE sample on the cavitational effectiveness, with respect to the degree of COD and TOC reduction and their degradation rates, samples were diluted and cavitated at the optimum inlet pressure of 500 kPa for 120 min . The original sample was diluted in two different proportions 25% and 50% (%V/V) using double distilled water and subjected to HC. Fig. 3 presents the % COD and % TOC reduction in comparison with the undiluted cavitated sample.

Table 3 presents the effect of dilution on the %reduction of COD and TOC with respect to increase in treatment time.Data in Table 3 indicates that the % dilution increased the % reduction rate of the COD and TOC reduction also increased. The degradation rate constant for COD reduction increased from 0.0016 to 0.0023 min_1 and for TOC reduction, it increased from 0.0013 to 0.0020 min-1 when sample was subjected to 50% dilution. The maximum COD and TOC reduction was 18.84% and 17.33% respectively obtained at 50% dilution which is slightly greater than the reduction obtained in undiluted sample. . The TDS reduction was negligible at 3.67% whereas the TSS reduction was 42.85% which corresponded to the effect of

significant effect of dilution on the mineralization of TWE. Therefore, it is not feasible to use dilution during the treatment of TWE using HC, as it will only increase the operational treatment costs because dilution will increase the total amount of the effluent to be treated. Moreover, the

biodegradability of the TWE samples was very low on dilution, as BI values ranged from 0.25 to 0.35 only. It is also evident from the earlier literature reported by Padoley et al. (2012) that dilution had no major impact on COD and TOC reduction of the wastewater using HC. Therefore, further studies were conducted without dilution of TWE at the inlet pressure of 500 kPa using HC.
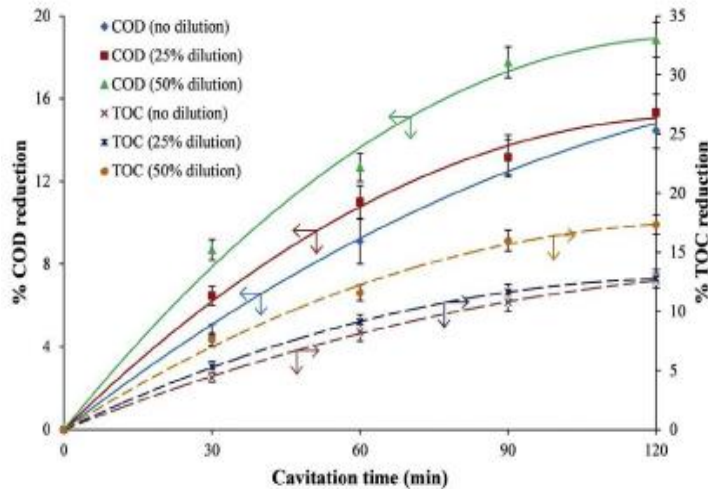

Fig. 3. Effect of dilution on COD and TOC reduction (Experimental conditions: sample volume, 7 L; inlet pressure

4.3. HC in combination with advanced oxidizing agent- ozone

In order to investigate the combined effect of HC +O3 on the treatment of TWE, different flow rates of O3 was introduced at the throat section of the cavitating device during HC. Experiments were conducted at four different mass flow rates of O3 i.e. 3 g/h, 5 g/h, 7 g/h and 9 g/h for 120 min at the optimized inlet pressure of 500 kPa. Fig. 4 presents the reduction in COD and TOC values at different dosage of O3 in 120 min of treatment time. It was observed from Table 4, that the % reduction in TDS was negligible (around 6%) whereas the % reduction in TSS increased from 36.18% to a maximum of 45.21% with an increase in mass flow rate of O3 from 3 g/h to 7 g/h. The % COD reduction increased from 15.97% to a maximum value of 26.81% as O3 dozing varied from 3 to 7 g/h and thereafter

TABLE 4

EFFECT OF HC+ OZONE DOSE ON PH, COD, TOC, TDS, TSS, BOD AND BI OF TWE

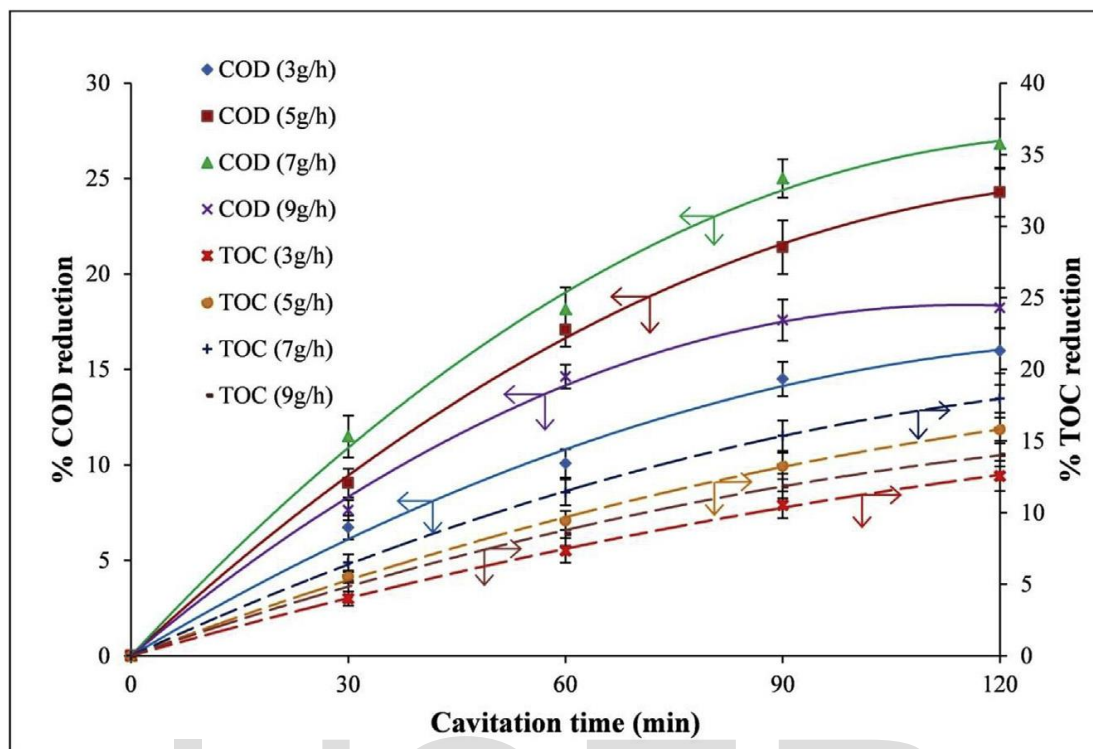| Parameters		HC + Ozone				
		HC only	HC + O$_3$ (3 g/h)	HC + O$_3$ (5 g/h)	HC + O$_3$ (7 g/h)	HC + O$_3$ (9g/h)
pH	Initial	7.35	7.21	7.30	7.31	7.40
	Final	7.54	7.50	7.56	7.53	7.48
COD (mg/L)	Initial	9680	9520	9720	9920	9440
	% reduction	14.46	15.97	24.28	26.81	18.22
	Quantum of reduction	1400	1520	2360	2660	1720
	Rate constant (min^{-1})	0.0016	0.0018	0.0028	0.0033	0.0023
	R^2	0.999	0.979	0.982	0.986	0.969
TOC (mg/L)	Initial	2349	2324	2389	2322	2336
	% reduction	12.60	12.56	15.82	17.96	14.04
	Quantum of reduction	296	292	378	417	328
	Rate constant (min^{-1})	0.0013	0.0012	0.0015	0.0018	0.0014
	R^2	0.986	0.988	0.983	0.973	0.975
TDS (mg/L)	Initial	20370	20050	19830	20160	18890
	% reduction	10.01	6.88	6.60	6.10	4.60
TSS (mg/L)	Initial	18950	18100	19100	17450	18050
	% reduction	34.82	36.18	41.09	45.21	43.82
COD/TOC	Initial	4.12	4.10	4.07	4.27	4.04
	Final	4.03	3.94	3.66	3.81	3.84
BOD (mg/L)	Initial	3200	–	–	3200	–
	Final	3600	–	–	3100	–
BI	Initial	0.33	–	–	0.32	–
	Final	0.43	–	–	0.42	–

Fig. 4.Effect of HC+Ozone on COD and TOC reduction (Experimental conditions: sample volume, 7 L; inlet pressure, 500 kPa).

decreased to 18.22% at higher O3 dozing of 9 g/h. The recombination reactions may have taken place in the presence of formation of excess radicals to form H2O2 and water which reduced the overall degradation rate. The maximum COD reduction of 26.81% and TOC reduction of 17.96% was observed with a degradation rate constant of 0.0033 min_1 and 0.0018 min_1 respectively at 7 g/h loading of O3 with HC. The increase in BI value from 0.33 to 0.43 was found to be the same for treatment by using HC alone as well as for HC combined with O3. This indicates favorable biodegradability of TWE by combining O3 with HC treatment. Table 4 presents that there has also been a decrease in COD/TOC ratio from 4.27 to 3.81 for the TWE sample treated at 7 g/h O3 dosing which indicates considerable reduction in TOC and corresponding COD.

4.4. HC in combination with advanced oxidizing agent- Hydrogen peroxide

The theoretical amount of H2O2 commonly used for the reduction of COD is 2.12 g of H2O2/g of COD (Bautista et al., 2008) however it primarily depends on the nature of the organic and inorganic content present in the TWE and their specific response to H2O2. The COD value of raw TWE was observed to be around 9 g/L and theoretically around 19-20 g of H2O2 will be required for its degradation. Batch studies conducted for the degradation of TWE effluent using H2O2 alone in a stirred tank mixer provided with normal stirring produced very low reduction in COD which indicated a very low dissociation of H2O2 into OH radicals by normal stirring and thereby low degradation efficiency. However, in order to examine the combined effect of H2O2 with HC, four different doses varying from 15 ml to 90 ml (i.e. equivalent to 2.38 g/L, 4.76 g/L, 9.51 g/L, 14.27 g/L) of H2O2 were introduced into the HC reactor prior to the cavitation process. Experiments were performed at the optimum inlet pressure of 500 kPa treating 7 L of undiluted sample for 120 min. Fig. 5 depicts the reduction in COD and TOC with respect to time for the various H2O2 dosages. Table 5 presents the reduction in TDS, TSS, BOD, COD and TOC and their respective degradation rate constants for the various dosages.

It was observed that the % reduction of TDS was decreasing with increase in H2O2 dosage. However, the % TSS reduction increased with increase in H2O2 dosing and had a maximum reduction of 49.60% for dose of 60 ml (i.e. 9.51 g/L). This indicates that the suspended particles are getting degraded into intermediates on reacting with H2O2 which are soluble and thereby increasing the TDS of the solution. The rate of reduction of COD and TOC increased with increase in H2O2 loading for the combined process in comparison to HC alone. Maximum reduction of 34.35% in COD and 19.71% in TOC was obtained for the H2O2 dose of 60 ml (i.e. 9.51 g/L) with corresponding degradation rate constants of 0.0043 min_1 and 0.0023 min_1 respectively. The process effectiveness will depend on the extent of production of hydroxyl radicals by the cavitation bubbles and the reaction of these radicals within and outside th

TABLE 5
EFFECT OF HC +H2O2 DOSE ON PH, COD, TOC, TDS, TSS, BOD AND BI OF TWE.

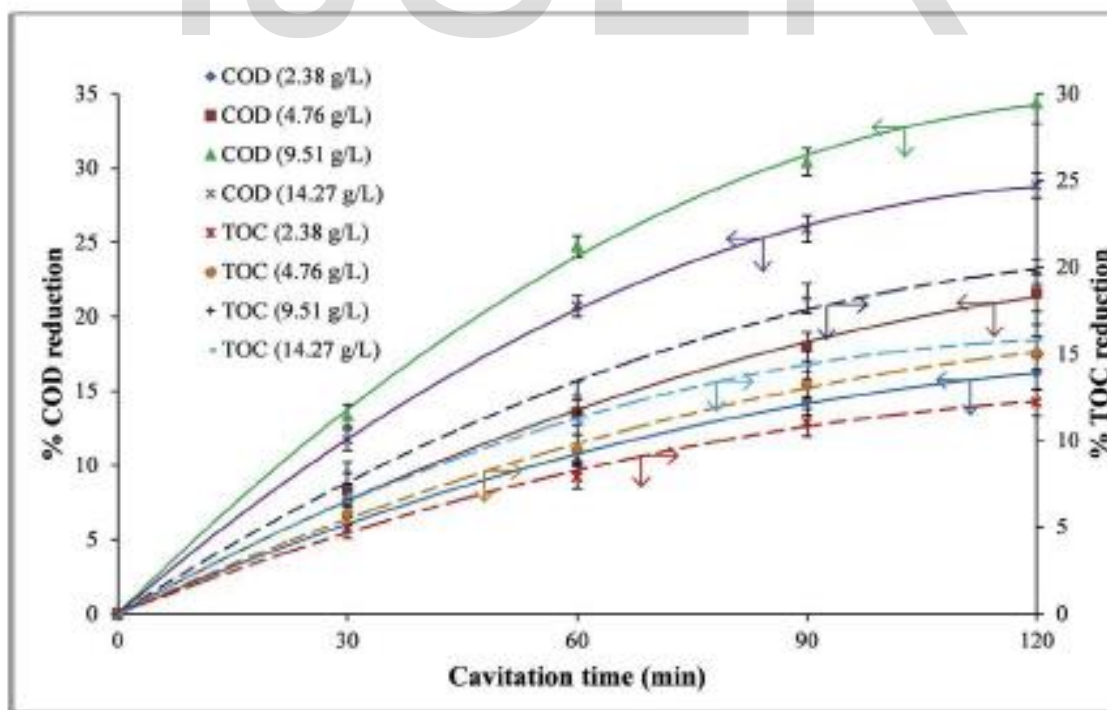| Parameters		HC + H₂O₂				
		HC only	HC + H₂O₂ (2.38 g/L)	HC + H₂O₂ (4.76 g/L)	HC + H₂O₂ (9.51 g/L)	HC + H₂O₂ (14.27 g/L)
pH	Initial	7.35	7.42	7.29	7.20	7.46
	Final	7.54	7.59	7.45	7.46	7.63
COD (mg/L)	Initial	9680	9380	9460	9140	8880
	% reduction	14.49	16.20	21.56	34.35	28.83
	Quantum of reduction	1400	1520	2040	3140	2560
	Rate constant (min⁻¹)	0.0016	0.0018	0.0023	0.0043	0.0035
	R²	0.999	0.979	0.980	0.980	0.979
TOC (mg/L)	Initial	2349	2263	2311	2374	2290
	% reduction	12.60	12.19	15.05	19.71	15.82
	Quantum of reduction	296	276	348	468	363
	Rate constant (min⁻¹)	0.0013	0.0013	0.0016	0.0023	0.0018
	R²	0.986	0.982	0.987	0.986	0.969
TDS (mg/L)	Initial	20370	19930	19070	18850	18770
	% reduction	10.01	8.47	7.86	7.10	4.95
TSS (mg/L)	Initial	18950	19130	18930	18750	19860
	% reduction	34.82	36.01	42.63	49.60	48.34
COD/TOC	Initial	4.12	4.14	4.09	3.85	3.88
	Final	4.03	4.00	3.78	3.14	3.28
BOD (mg/L)	Initial	3200	–	–	2800	–
	Final	3600	–	–	2500	–
BI	Initial	0.33	–	–	0.30	–
	Final	0.43	–	–	0.41	–
H₂O₂ (g)/COD (g)		–	1.57	2.33	3.02	5.57
H₂O₂ (g)/TOC (g)		–	8.62	13.68	20.32	39.31

Fig. 5.Effect of HC+ H2O2 on COD and TOC reduction (Experimental conditions: sample volume, 7 L; inlet pressure, 500 kPa)

bubbles by the various organic/inorganic species present in the TWE sample. However, excess dosing of H2O2 caused the scavenging of the hydroxyl radicals and therefore the % reduction in COD and TOC decreased at the H2O2 dosing of 14.27 g/L. First order rate kinetics was fitted for the COD and TOC reduction and a maximum degradation rate constant of 0.0043 min_1 and 0.0023min_1 was obtained for the % reduction in COD and TOC respectively at the optimized H2O2 loading for the hybrid process. Similar results have been reported on the degradation of imidacloprid by Raut-Jadhav et al. (2016a) using circular venturi HC and on the degradaxtion of Rhodamine 6G using slit venturi by Rajoriya et al. (2017a) and for the treatment of 2,4,6- trichloro phenol (TCP) using HC + H2O2 by Barik and Gogate (2018) respectively

4.5. Combined effect of HC and Fenton's reaction

The concentration of the Ferrous salt (FeSO4.7H2O) and the dosage of H2O2 into the HC reactor are the two deciding factors for the combined HC þ Fenton process efficiency. The initial pH of the TWE was around pH 7.4 ± 1. On addition of H2O2 and FeSO4.7H2O into the TWE, the drop in pH was observed up to a pH of 6.7 ± 1, which may be due to the production of organic acids from the fragmentation of organic molecules by the hydroxyl radicals. However, when the samples were subjected to cavitation, the pH of the samples again increased to a value of 7.5 ± 1. The experiments were performed using the optimized dose of H2O2 (i.e. 9.51 g/L) which brought the maximum reduction of COD in the HC þ H2O2 study and kept constant for all the ratios of FeSO4 to H2O2. The doses of FeSO4.7H2O were 0.5 g/L, 1 g/L, 3 g/L, 5 g/L (equivalent w/w ratio of FeSO4.7H2O to H2O2 is 1:19, 1:10, 1:3, 1:2) added to 7 L of the TWE sample which was cavitated in the HC reactor at 500 kPa inlet pressure for 120 min. The degradation efficiency was studied in terms of reduction obtained in TDS, TSS, COD, BOD and TOC Fig. 6 presents the % reduction in COD and TOC values at varying doses of ferrous sulfate in 120 min of treatment time and presented in Table 6.

It was observed that as the loading of ferrous sulfate increased, reduction in COD and TOC also increased until the optimum loading of 3 g/L i.e. for H2O2/FeSO4.7H2O ratio of 3:1. Thereafter there was a

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decrease in the reduction in COD and TOC which may be

due to the auto scavenging of the hydroxyl radicals by ferrous ion itself at higher concentrations. The first order rate kinetics was also fitted for the reduction of COD and TOC and the data is given in Table 6. The maximum of 50.20% COD and 32.41% TOC reduction was observed at H2O2/FeSO4.7H2O ratio of 3:1, and with a rate constant of 0.0071 min_1 and 0.0042 min_1 respectively. Moreover, Fenton oxidation in combination with HC also increased the biodegradability of wastewater as its BOD/COD ratio increased from 0.28 to 0.46, which is an increase by 64% compared to an increase by 30% using HC alone. The improved biodegradability observed is associated with the partial oxidation of TWE effluent to give low molecular weight oxygenated compounds rather than complete mineralization to carbon dioxide. Fenton's process alone for treatment of TWE was also conducted using the optimized doses of ferrous sulfate (3 g/L) and H2O2 (9.51 g/L). After 120 min, 24.52% reduction was observed in COD with degradation rate kinetics having a first order rate constant of 0.0025 min_1. The consumption of H2O2 (g) per g of COD and TOC for Fenton process alone was 4.14 g/g and 31.92 g/g respectively. The requirement of H2O2 per g of COD reduction for the hybrid process of HC þ Fenton has reduced from 4.14 to 1.95 g/g. Similarly, the consumption of H2O2 per g of TOC reduction was reduced from 31.92 g/g to 11.89 g/g. It has been observed that application of Fenton alone is not advantageous as it requires higher dosage of H2O2 and ferrous sulfate which may also induce coagulation and problems of excessive sludge formation especially for complex effluents like TWE which require high oxidant dosing. Whereas in the hybrid process of Fenton combined with HC, the physical and chemical effects of cavitation created a synergistic mechanism enhancing the degradation efficiency of TWE with reduced amount of H2O2.

5.CONCLUSIONS

This study proved that the hybrid treatment techniques of using HC in combination with three oxidation agents i.e. O3, H2O2 and Fenton's reagent provided intensified treatments with higher degradation efficiencies and an increase in the BI value, making the treated tannery wastewater more suitable for biological treatment.When the tannery wastewater was subjected to HC treatment alone at the optimum pressure of 500 kPa for 120 min, maximum reduction of 14.46% COD and 12.6% TOC was obtained along with a reduction in TDS and TSS, and an increase in BI value from 0.33 to 0.43 due to the breaking down of the more recalcitrant organic molecules into biologically degradable compounds. However, wastewater dilution did not enhance the HC degradation efficiency and therefore it is not feasible as it only increases

the operational costs due to the processing of larger volumes.

TABLE 6

EFFECT OF HC+ FENTON'S REAGENT ON PH, COD, TOC, TDS, TSS, BOD AND BI OF TWE.

Parameters		HC + Fenton's [(Ferrous dose; g/L), [FeSO$_4$7H$_2$O:H$_2$O$_2$ w/w]]				
		HC only	HC + Fenton's (0.5 g/L) [1:19]	HC + Fenton's (1.0 g/L) [1:10]	HC + Fenton's (3.0 g/L) [1:3]	HC + Fenton's (5.0 g/L) [1:2]
pH	Initial	7.35	7.40	7.40	7.31	7.31
	Final	7.54	7.47	7.53	7.45	7.39
COD (mg/L)	Initial	9680	9640	9640	9760	9760
	% reduction	14.46	23.03	32.78	50.20	46.93
	Quantum of reduction	1400	2220	3160	4900	4580
	Rate constant (min^{-1})	0.0016	0.0028	0.0043	0.0071	0.0061
	R^2	0.999	0.944	0.952	0.961	0.963
TOC (mg/L)	Initial	2389	2398	2398	2468	2468
	% reduction	12.60	17.26	23.68	32.41	28.81
	Quantum of reduction	296	414	568	800	711
	Rate constant (min^{-1})	0.0013	0.0019	0.0026	0.0042	0.0032
	R^2	0.986	0.975	0.970	0.974	0.991
TDS (mg/L)	Initial	20370	18450	18450	19180	19180
	% reduction	10.01	4.82	3.30	1.88	1.15
TSS (mg/L)	Initial	18950	17700	17700	19950	19950
	% reduction	34.82	40.96	45.48	53.88	45.86
COD/TOC	Initial	4.12	4.02	4.02	3.95	3.95
	Final	4.03	3.74	3.54	2.91	2.95
BOD (mg/L)	Initial	3200	–	–	2800	–
	Final	3600	–	–	2400	–
BI	Initial	0.33	–	–	0.28	–
	Final	0.43	–	–	0.46	–
H$_2$O$_2$ (g)/COD (g)		–	4.28	3.01	1.95	2.07
H$_2$O$_2$ (g)/TOC (g)		–	22.97	16.75	11.89	13.38
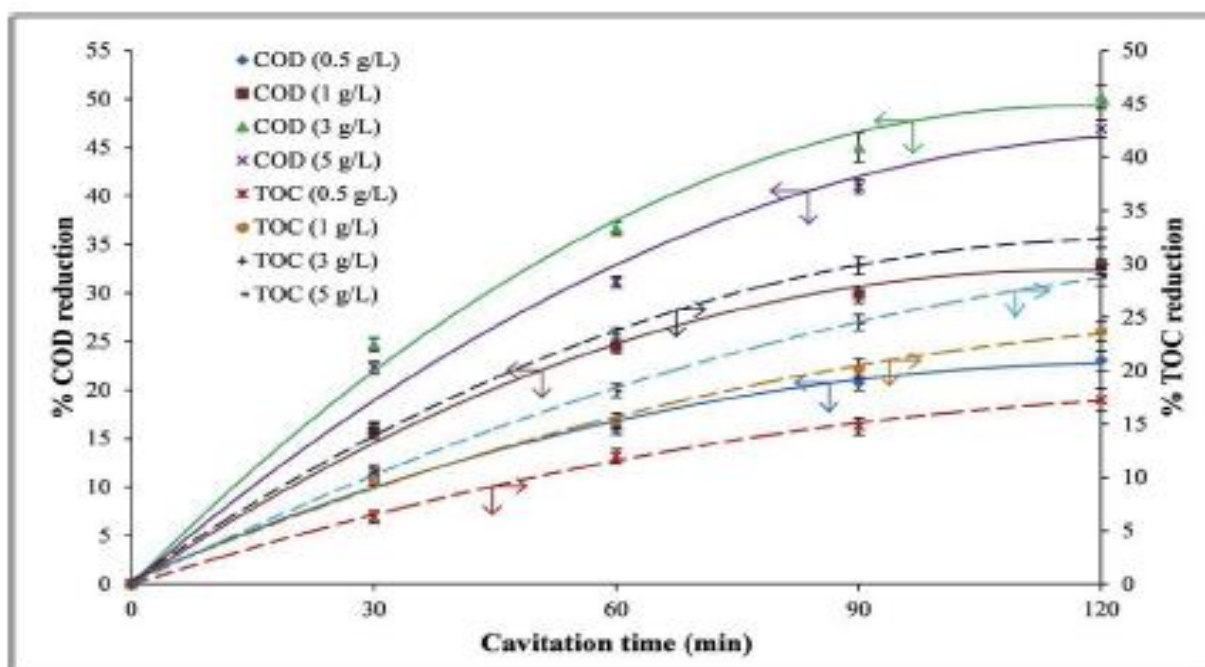
9.51 g/L).

HC +Fenton's process caused a maximum reduction of 50.20% COD and 32.41% TOC respectively at FeSO4.7H2O/ H2O2 ratio of 1:3 (w/w). The extent of COD reduction was found to increase two-fold in case of HC + O3 and HC +H2O2,whereas it showed a 3.5-fold increase for HC +Fenton compared to HC alone. Moreover, the maximum degradation efficiency was observed in case of the hybrid HC + Fenton process with higher BOD, COD, TSS reduction and less consumption of H2O2. It was observed that the consumption of H2O2 per g of COD and TOC reduction for HC + Fenton was lesser at the rate of 1.95 g/g and 11.89 g/g whereas in the case of HC +H2O2 it was 3.02 g/g and 20.32 g/g respectively at optimized conditions. Therefore, hybrid HC + Fenton showed the highest synergetic energy efficiency and cost effectiveness than HC and other hybrid processes. Therefore, hybrid HC oxidation methods considered as clean technology can be combined with biological treatment processes to bring treated water characteristics to conditions within the prescribed permissible limits for reuse or discharge in environment.

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