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DEGRADATION STUDIES ON ANIONIC AND NON-IONIC SURFACTANTS BY OZONATION

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ABSTRACT

A lab scale study on the degradation of anionic and non-ionic surfactants in aqueous solution was carried over by ozonation in order to study the effect of ozonation and its operational variables such as ozone concentration, ozonation time and ionic nature of surfactants. Two types of surfactants namely Sodium Dodecyl Sulphate (SDS) an anionic surfactant and Tween 80 (T80) a non-ionic surfactant were taken and the degradation was recorded in terms of their Critical Micille Concentration (CMC) values, Chemical Oxygen Demand (COD) and absorbance for spectrum light. In terms of CMC the residual surfactant concentrations after ozonation were about 4 mg/L in the case of SDS and 1.25 mg/L for T80. In absorbance study the degradation efficiency was noted to be about 86.67%for SDS and 97.14% for T80 and the residual concentrations were found to be 4 mg /L and 2mg/L respectively. COD reduction was measured as 73% and 77% for T80 and SDS respectively.

INTRODUCTION

Surfactants are most widely used components in the detergent industry. Surfactants are organic compounds consisting of two parts: water loving (hydrophilic) portion and a water-hating (hydrophobic) portion (Rosen, 1989). Surfactants degradation is a must, as because its toxicity is of concern now days in water contamination. The main character of the surfactant is that the hydrophobic portion so called the tail gets attached to the toxic components

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in the water and thus enhances the toxicity (Swisher, 1970). Surfactants degradation can be carried out by various methods, like chemical or biological. But some of the surfactants are highly recalcitrant and thus cannot be biodegraded. Biodegradation cannot be employed for certain surfactants; it is time consuming and needs several pre-treatment processes. Adsorption or photo-catalysis can be used as an alternative but it does not totally eliminate or degrade the surfactant components.

Several studies have been employed on removal and degradation of surfactants present in effluents. It has been reported that about 91% of Alkyl Benzene Sulphates (ABS) and almost 99.50% removal of Dodecyl Benzene Sulfonate (DBS) was attained in activated carbon adsorption for surfactant concentration of 15 ppm at solution pH 3 (Nayyar *et al.* 2004). Biodegradability studies have also been employed on surfactants in which Anoxic fixed bed reactor has been employed to biologically degrade the Linear Alkyl Sulphate (LAS), which reduced from 100µl to 20µlwith detention time of 10 days (David Schleheck, 2003).

In a kinetic study of photocatalytic degradation of Cetyl Pyridinium Chloride, a cationic surfactant with TiO_2 the degradation rate was measured as 6-7x10^2 m mol/g catalyst /min with catalyst loading rate of 0.5g/L of surfactant sample (Yong Eng *et al.* 2000) and on Polyoyethylene, a non ionic surfactant the degradation rate was found to be proportional to TiO_2 surface area and square root of UV high intensity and independent on the initial concentration of surfactant (Kimura, 2004)

Ozone is used for many applications in environmental engineering like disinfection of drinking water, inactivation of viruses and industrial wastewater reclamation (Venkata Rao, 1997). Ozonation has been employed in the treatment of secondary treated effluents (Kanimozhi R 2004); treatment of dyes form textile industries (Strickland *et al.* 1995) decomposition of hazardous chemical substances in organic solvents; in treatment of pesticides etc and have been found to be effective. Ozonation process has been used as a pretreatment before biodegradation process for removal of recalcitrant compounds like Polycyclic Aromatic Hydrocarbon (PAH).

Continuous ozonation on polycyclic aromatic hydrocarbons (PAH) such as benzo (e) pyrene and benzo(k)fluoranthene were oxidized followed biological treatment and reported that by improving ozone mass transfer rate the PAH oxidation rate could be increased (Kornmuller, *et al.* 1999). Ozonation on Kraft bleach plant effluent removed 90% color easily with the ozone concentration of 600 ppm and addition of 100 ppm hydrogen peroxide reduced the ozone consumption to 300 ppm for the maximum removal (Prat *et al.* 1988). Decolorization of spent reactive dye bath of azo and azo free dyes was achieved upto 99% and 90% using ozonation and UV/H_2O_2 respectively (Takahashi, 1996). Ozone and ozone/hydrogen peroxide were used in combination with a granular activated carbon containing column to assess the effectiveness as a post treatment option for UASB treated fruit cannery and winery effluent and found that the color reduction in the effluents ranged from 66% to 90% and COD reduction of 27-55% were achieved Sigge *et al.* 2002). Color removal from biologically treated molasses wastewater by means of chemical oxidation

with ozone has been reported as 71% to 93% and COD reduction from 15% to 20% were reached after 30 min reaction time without change in TOC values (Pena *et al.* 2003).

Materials used
Experimental set-up

The units used for the experimental set up were Ozonator, air compressor, bubble column reactors and air diffuser and the set-up is shown in Figure. 1.

Ozonator

The Ozonator used for the study was CDS 2G INDIZONE model supplied by ozone Technologies and Systems India Ltd., Chennai, which could produce 2% ozone if fed with air. The voltage applied was 220V.

Air compressor

Centrifugal pump type air compressor capable of working at a pressure up to 1 kg/cm^2 were used to supply air for ozonation.

Bubble columns reactors

3 Nos of "Pyrex" glass columns of 4.8 cm diameter and 45 cm in height were used. Each column has the provisions for gas (ozone) inlet; outlet and sampling ports for taking effluent from the reactor. The gas diffuses through porous diffuser stones.

Other instruments

Surface tensio meter, pH meter, Spectrophotometer, and COD digester were also used for the characteristics analyses of samples.

Chemical reagents

AR grade synthetic surfactant samples Sodium Dodecyl Sulphate and Tween 80 samples were supplied by HI-Pure Chemicals and CDH.

METHODOLOGY

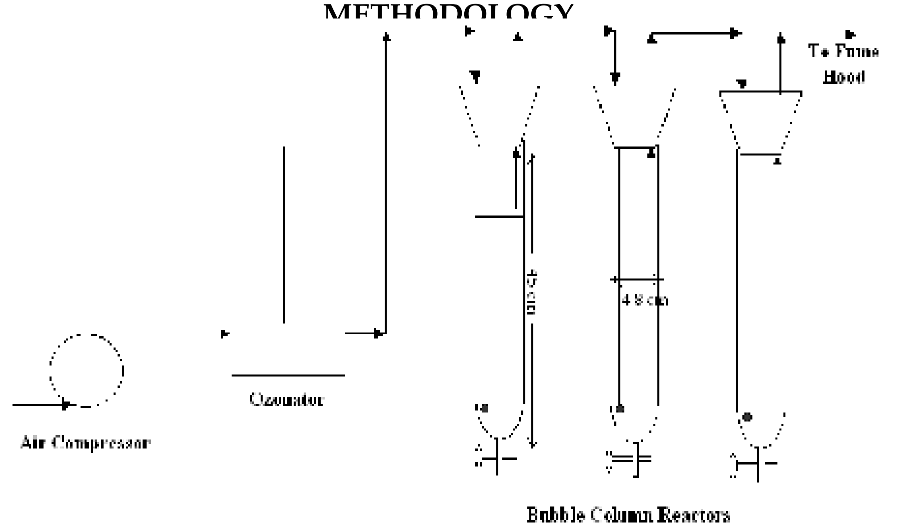

Fig. 1 Schematic representation of Experimental set-up

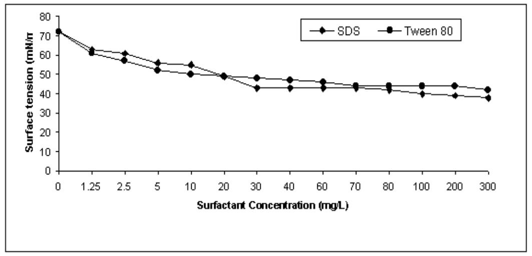

Fig. 2 Critical Micelle Concentration of Surfactant

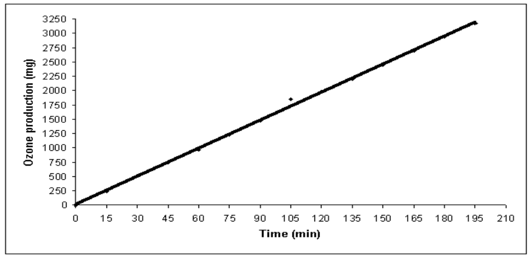

Fig. 3 Calibration graph of the ozonator

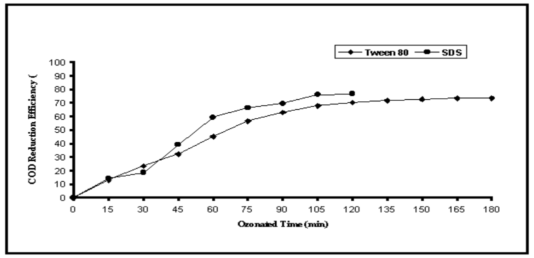

Fig. 4. Effect of Ozonation on COD Reduction

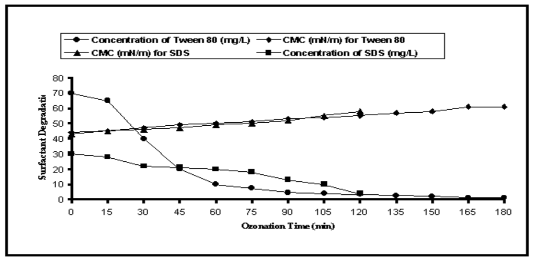

Fig. 5 Effect of Ozonation on CMC

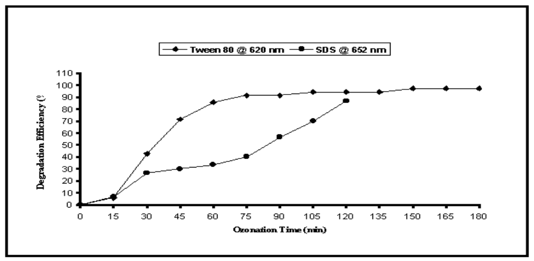

Fig. 6 Effect of Ozonation on Absorbance

Estimation of critical micelle concentration of surfactants

Critical Micelle Concentration (CMC) was estimated to know at which particular concentration the surfactant reduces the surface tension extremely well. A standard plot made of surfactant concentration vs surface tension was used to estimate the CMC.

The surfactant concentration of SDS and T80 samples were determined by diluting the sample until the surface tension measured was above the minimum surface tension. The concentration was then determined using the standard plot and multiplying by the appropriate dilution factor.

The estimated CMC values of anionic surfactant SDS was 30 mg/L which is more toxic than that of non-ionic T80 whose CMC value was 70 mg/and the results are depicted in Figure 2.

Calibration of ozonator

The ozonator used for the study was calibrated at the airflow rate of 1Kg/cm^2. The average rate of ozone production at the operating flow rate was obtained to be 0.9g/h. The calibration was checked periodically and the calibration graph is depicted in Figure 3.

RESULTS AND DISCUSSION

Effect of ozonation on chemical oxygen demand

It was observed that COD reduction of 73% was achieved by ozonation in case of T80 surfactant wastewater and that of SDS was 77%. The maximum COD reduction occurred during 90 to120 minutes and 60 to 105 minutes for T80 and SDS solutions respectively, from then, there was only a gradual decrease on the COD concentration and the decline was negligible. The residual COD of ozonated effluents were 33 mg/L and 43 mg/L for T80 and SDS wastewaters respectively. The results are shown in Figure 4.

Effect of Ozonation on CMC

Ozonation reduced the surfactant concentration in the synthetic solution samples. The CMC value and the surfactant concentration are inversely proportional as the CMC value increases the surfactant concentration decreases (Figure 5). The ozonation time increased with CMC value and the surfactant concentration gradually decreased. The residual CMC values of the ozonated samples were 58 mN/m for T 80 and 61mN/m for SDS wastewaters and the surfactant concentration after ozonation was about 4 mg/L for SDS and 1.25 mg/L for T 80 after a time interval of about 120 and 180 minutes respectively.

Effect of Ozonation on absorbance

Absorbance at 620 nm and 652 nm for non-ionic surfactant and anionic surfactant respectively represents the surfactant concentration in the sample.

There was a gradual decrease in the concentration of the surfactant from 30 mg/L to 4 mg/L in the case of SDS surfactant wastewater and was from 70 mg/L to 2mg/L for T 80 with an ozonation time of about 120 and 180 minutes respectively.

In the case of Tween 80 surfactant wastewater, the degradation efficiency was about 91.42% at 75 minutes of ozonation time and after that the degradation was very gradual and the degradation efficiency was about 97.14% at 180 minutes ozonation time, which is of negligible amount after such a prolonged ozonation time as well as high ozone concentration. Same condition was also found for SDS surfactant wastewater, where in the degradation efficiency of 70% was achieved in 105 minutes and then after 120 minutes the degradation efficiency was about 86% with a residual surfactant concentration of 4 mg/L. The results have been depicted in Figure 6.

CONCLUSIONS

In comparison with other Advanced Oxidation Processes like photocatalytic process, ozonation required only about 50% of contact time to achieve maximum degradation and the ozonation does not required to adjust pH. Ozonation of surfactants also reduces the COD of surfactant wastewater to about 75% within 1.5 to 2 hours contact time. To attain maximum COD reduction in Tween 80 it required 4.4 g of ozone per litre of the sample and for SDS, the same was 2.5g per litre of sample.

During ozonation degradation was initially rapid and linear to a stipulated time after which it became slow and sustained. Though the surfactant content in the wastewater decreased as ozonation time increased, a notable degradation of about 65-70% is achieved within 50-75% of total contact time. As the CMC value increases, the surfactant concentration decreases, Ozonation process is capable of achieving higher CMC values for the surfactant wastewater samples, during the course of ozonation time. Hence it is concluded that Ozpnation may be a viable technology in treatment of wastewaters having surfactants. However pilot scale and economic studies have to be conducted for further field levels.

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