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Solar Photocatalytic Degradation of Biomethanated Distillery Spentwash using Semiconductor Metal Oxide Nanoparticles

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Abstract: *Advanced oxidation processes (AOPs) are emerged technologies characterized by ability of in-situ generation of hydroxyl radical, well known for its high capacity of degradation of recalcitrant contaminants. Wastewater from sugar industry contains a considerable amount of toxic organic load which are most harmful to the environment. Primary treatment processes only involves separation rather than treatment of distillery wastewater. Heterogeneous photocatalysis is one of the most powerful advanced oxidation processes. Distillery spentwash consists of different pollutants that includes caramels, phenols, melanoidins etc. different complex organic molecules. Biomethanated spent wash was obtained from Vasandada sugar institute.The degradation studies were carried out by diluting the Biomethanatedspentwash. Biomethanatedspentwash was analyzed by COD analysis system. In the present investigation, we have constructed solar photoreactor for the degradation of the biomethanated distillery spentwash. Photocatalytic degradation was carried out under normal sunlight with help of solar photoreactor. The average solar intensity was 19mW/cm^2 measured at 365nm.The various Photocatalysts used were Degussa P25 TiO_2, Merck TiO_2, Prepared TiO_2, Prepared Ag- TiO_2, and Merck ZnO.*
Keywords:*Photocatalysis, Spentwash, Degradation, AOP and TiO_2*

1.Introduction:

Wastewater from the sugar industry contains a considerable amount of toxic organic load and many of them are recalcitrant compounds harmful to the environment[1,2,3]. The recalcitrant nature of distillery spentwash is due to the presence of the dark brown colorants which are biopolymeric colloidal materials that are negatively charged[4,5]. Except caramel, all colorants contains phenolic groups which contribute to their formation. Infrared spectra of alkaline degradative products indicate the presence of high molecular weight aminoacids[6]. It has been suggested that most of the phenolic colorants are derived from benzoic acid and cinnamicacid, that are precursors of flavanoids, the yellow pigments of the plants responsible for the color formation.

The unpleasant odor of the effluent is due to the presence of skatole ,indole and other sulfur compounds which are not decomposed by yeast during distillation[6]. During heat treatment, maillard reaction takes place resulting in formation of melanoidins one of the final products of the maillardreaction[7].

Apart from melanoidins, the other recalcitrant compounds present in the waste are caramel, different products of sugar decomposition, anthocyanins, tannins and different xenobiotic compounds. Melanoidins are dark brown to black colored natural condensation products of sugars and aminoacids, they are produced by non- enzymatic, browning reactions known as maillardreactions[8].

The structure of melanoidins is still not completely understood but it is assumed that it does not have a definite structure but, it largely depends on the nature and molar concentration of parent reacting compound and reaction conditions as pH, temperature, heating time and solvent system used[9]. melanoidins also have antioxidant properties which render them toxic to many micro-organisms such as those typically present in the wastewater systems. The resistance of melanoidins to degradation is apparent from the fact that these compounds escape various stages of wastewater treatment plants and finally enters into environment[10].

Sugarcane molasses based distillery wastewaters disposal into the environment is hazardous and has high pollution potential[11]. High COD, Total nitrogen and total phosphate content of the effluent may result in eutrophication of natural water bodies. The highly colored components of the molasses wastewater reduce sunlight penetration in rivers, lakes or lagoons which in turn decreases both photosynthetic activity and dissolved oxygen concentration affecting aquatic life[12]. Disposal of sugarcane molasses wastewater on land is equally hazardous to the vegetation. It was reported to reduce soil alkanity and manganese availability thus inhibiting seed germination[13]. Several technologies have been explored for reducing the pollution load of sugarcane molasses wastewater. Majority of these methods decolorize the effluent by either concentrating the color into sludge or by breaking down the colored molecules[14]. Several conventional processes have currently been used in the sugar industries such as coagulation, flocculation, incineration, microbial degradation and adsorption on activated carbon[15-19].

Advanced oxidation processes (AOPs) have emerged out as technology for wastewater treatment. AOPs involves generation of hydroxyl radical, well known for its high capacity of degradation[20]. Heterogeneous photocatalysis using semiconductor metal-oxide is promising AOP for the treatment of wastewater effluents[21]. In current study we have used metal oxide semiconductor (TiO_2 and ZnO) and its composite for the degradation of biomethanated distillery spent wash.

1.1. Materials and Method:

TiO_2 and ZnO were ordered from Merck India. Evoniks P25 (Degussa P25) was gifted from Evoniks. Prepared TiO_2 and Ag-TiO_2 were prepared as discussed in the our earlier paper[22,23]. Biomethanated spent wash (BDSPW) was obtained from Vasandada sugar Institute (VSI) Pune.

UV Reactor : The photocatalytic reaction system included a 500mLcylindrical glass reactor, inside equipped with a UV illumination source (254 nm), which was located axiallyand held in a quartz immersion tube as shown in figure 1. A circulating water jacket was employed to cool the irradiation source, thuspreventing any heating of the suspension[24]. Air was bubbled through the reaction solution from the bottom using aeratorwith constant speed. In a typical photocatalytic test performed at room temperature, 200 mg photocatalyst wasadded into 500mL of diluted biomethanated distillery spent wash solution.

Solar Reactor :The solar photocatalytic reactor as shown fig 2 wasused to degrade Biomethanated distillery spent wash[25]. The reaction mixture was passed through the reactor such that total concentration of the catalyst used was 0.4g/L. The bed of reactor consisted of aluminum reflector. A peristaltic pump was used for continuous circulation of BDSPW between the reservoir tank and solar reactor. The BDSPW was circulated with photocalayst Powder as mentioned in the photoreactor under normal sunlight in summer (in the month of May). The average intensity of sunlight at 365nm was found to be 19 mW/cm^2.

The amount of pollutant degraded was analyzed by COD analysis. COD method was performed using Spectralab COD titrator using open reflux method.

Figure 1: UV Photocatalytic reactor

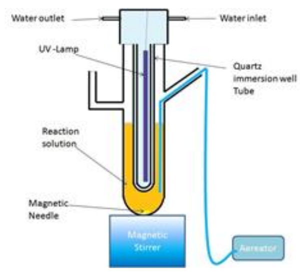
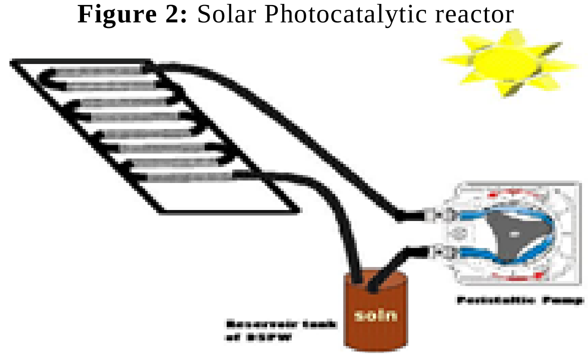


Figure 2: Solar Photocatalytic reactor



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2. Results and Discussion:

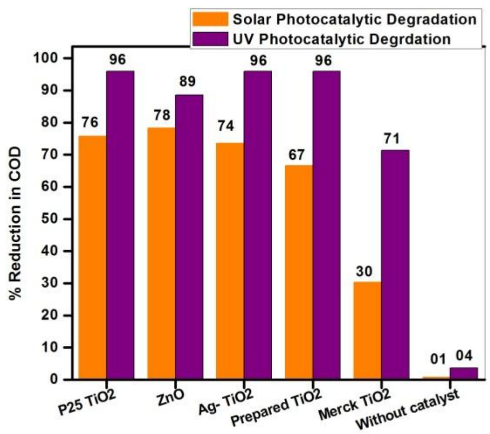
The different Photocatalyst used for the distillery spent wash degradation are as shown in the table below with the values of their surface area.

Table 1: BET Surface area photocatalyst used

Catalyst	Surface area m^2/g
Prepared TiO_2	150
Prepared Ag-TiO_2	140
Merck TiO_2	6.4
Degussa P25 TiO_2	50
Merck ZnO	5

It can be seen that surface area of prepared TiO_2 is high as compared to others. Prepared TiO_2 and Prepared Ag-TiO_2 contains pure anatase phase.Merck TiO_2 also contains pure anatasephase[22,23]. Degussa P25 TiO_2 contains 20:80 mixture of rutile and anatase respectively. ZnO is containing wurzite structure.

Figure 3: Percencentage COD Reduction of different photocatalysts used for photocatalytic degradation of biomethanated distillery spent wash under UV and Solar irradiation



From the figure 3, it was found that the Degussa P 25 $TiO_2$and ZnO showed very good photocatalytic activity under natural sunlight. Amongst Prepared $TiO_2$and Ag-TiO_2,Ag-TiO_2showed better photocatalytic activity than Prepared TiO_2. Merck TiO_2 showed very less photocatalytic activity for the degradation of spent wash.

As the both TiO_2 and ZnO have maximum absorption in UV range the photocatalytic activity is high in UV light compare solar Light.

Photocatalytic activity for degradation of biomethanated distillery spent wash depends on factors such as type of energy used, surface area and electron-hole suppression in photocatalyst.

ZnOShows highest photocatalytic activity though it is having very low surface area. ZnO is having high electron mobility, due to which there is generation of large amount of H_2O_2utilised for oxidation of pollutant[26].Commercially available Degussa P25 is prepared byhydrolysis of $TiCl_4$ in hot flame to give a mixture of 80%anatase and 20% rutile TiO_2. The method of preparationand composition of Degussa P25 are mainly responsible forits higher photocatalytic activity. The higher photocatalytic is due to suppression of electron-hole recombination.The better photocatalytic activityshown by Ag-TiO_2 over the prepared TiO_2 can beexplained on the basis of silver being an acceptorimpurity in doping of TiO_2, it acts as an electron trapand prevents the electron hole recombination, which isimportant factor in determining the photocatalyticactivity. The probable reason behind the enhancement of photocatalytic activity of as prepared TiO_2 as compared to Merck TiO_2 can be attributed its high surface area.

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