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Treatment of petroleum industry wastewater using TiO_2/UV photocatalytic process

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Abstract : In the present study, degradation of petroleum industry wastewater has been investigated through laboratory experiments by employing heterogeneous photocatalytic process. A photocatalytic reactor was used for the advanced oxidation. The industrial wastewater was characterized. Photocatalytic activity of semiconductor such as titanium dioxide (TiO_2) has been investigated. An attempt has been made to study the effect of process parameters through amount of catalyst, and operating pH on photocatalytic degradation of petroleum industry wastewater. The experiments were carried out by varying pH (2–11), amount of catalyst (0.25–1.5 g/L). Optimal suspended catalyst concentration, fluid pH and temperature were obtained at amounts of near 1 g/L, 3 and 50 °C, respectively. The maximum rate of degradation was observed in acidic medium at pH 3 and maximum reduction in chemical oxygen demand (COD) of 60%.

Keywords : Wastewater, photo-catalysis, photocatalytic degradation, COD, TiO_2.

Introduction

Huge amounts of water are used in a petroleum refinery and, consequently, significant volumes of wastewater are generated. The traditional treatment of refinery wastewater is based on the physicochemical and mechanical methods and further biological treatments in the integrated activated sludge treatment units. The contamination of water supplies by organic molecules is an increasing problem mainly because many of these molecules are not readily degraded by conventional methods for the treatment of effluents[1]. Besides causing visual pollution, this kind of pollutant has high levels of toxicity, non-biodegradability and resistance to destruction[2]. Several solutions are proposed in this regard, including use of coagulation enhanced by centrifugation, ultra filtration[3] or sorption on organ minerals[4] with a level of advantage for each. These methods are not efficient and cost effective for wastewaters containing high concentration of more toxic pollutants. This requires some novel techniques to transfer the highly toxic pollutants chemically into benign species. Advanced oxidation processes (AOPs) are more efficient, cheap, and ecofriendly in the degradation of any kind of toxic pollutants. These processes can completely degrade the organic pollutants into harmless inorganic substances such as CO_2 and H_2O under moderate conditions. AOPs generate hydroxyl radical, a strong oxidant, which can completely degrade or mineralize the pollutants non-selectively into harmless products[5].

Titanium dioxide (TiO_2) is generally considered to be the best photocatalyst and has the ability to detoxificate water from a number of organic pollutants. However widespread use of TiO_2 is uneconomical for large-scale water treatment, thereby interest has been drawn toward the search for suitable alternatives to TiO_2 [6]. Many attempts have been made to study photocatalytic activity of different semiconductors such as SnO_2, ZrO_2, CdS and Nb_2O_5 [7], compared the photocatalytic activity of TiO_2, SnO_2, ZnS, Nb_2O_5 and CdS for the degradation of petroleum wastewater and found TiO_2 to be the most effective catalyst.

Experimental

Chemicals :

Titanium dioxide (99.7%) was used as a photo catalyst and purchased from Molychem, India. The wastewater was collected from petroleum industry. Distilled water was used for preparation of various solutions. pH of the solutions was adjusted with 1 *N* H_2SO_4 or 1 *N* NaOH. All others chemical used were of analytical grade.

Characterization of the wastewater :

The petroleum industry wastewater samples were obtained, after pretreatment and before the treatment. Composition of the wastewater used in this study was analyzed before the experimental studies. The pH values of the effluent samples used in the experimental studies. The characteristics of petroleum industry wastewater are shown in Table 1.

Table 1. Characteristics of petroleum industry wastewater

Parameter	Raw effluent
pH	4.5
Turbidity (NTU)	450
TDS (mg/L)	578
Conductivity (s/m)	122
TSS (mg/L)	468
Carbonate (mg/L)	Nil
Dissolved oxygen (mg/L)	1.8
Chlorine demand (mg/L)	1.9
COD	8200

Experimental setup and procedure :

The photo-catalytic degradation was carried out in batch reactor as shown in Fig. 1. The light source was 400 W UV lamp in the range 200–550 wavelengths. For the degradation experiments, fixed amount of photo catalyst TiO_2 was added to 500 mL of wastewater in each run at definite pH. The suspension was subjected to irradiation under UV light and starring with help of magnetic stirrer for a fixed interval of time. At different time intervals, a sample was taken out with the help of a pipette and then centrifuge to remove the catalyst. The removal efficiency (% Removal) was calculated from the following formula :

$$\% \text{ Removal} = [(COD_i - COD_f)/COD_i] \times 100$$

where COD_i and COD_f stands stand the initial and after any irradiation time, COD values.

Fig. 1. Experimental setup for degradation of petroleum industry wastewater.

Analytical analysis :

The COD test was performed by Wet Chemical Oxidation method. It is used to measure the oxygen demand for the oxidation of organic matters by a strong chemical oxidant which is equivalent to the amount of organic matters in sample.

Results and discussion

The experiments were carried out to study the degradation wastewater employing TiO_2 as catalyst under UV light. Various parameters which affect the removal efficiency such as catalyst loading (0.25–1.5 g/L), pH (2–11) and were assessed under UV light.

Effect of catalyst concentration :

Fig. 2 shows the effect of catalyst loading (TiO_2) on the degradation of petroleum industry wastewater. Almost no pollutant elimination was achieved with UV light

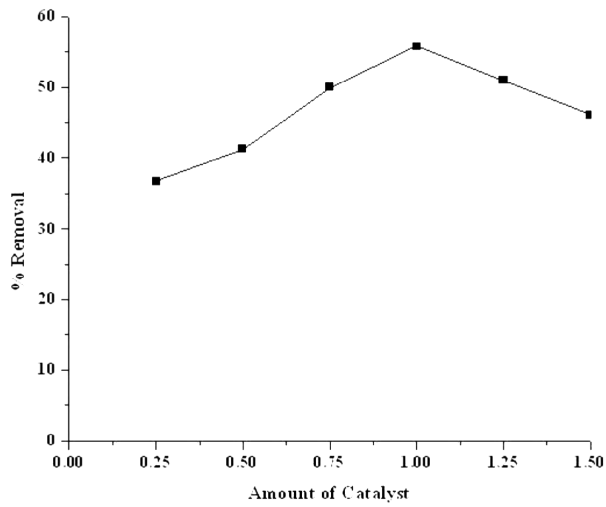

Fig. 2. Effect of catalyst concentration on degradation of wastewater.

alone, while results show the significant degradation in the presence of catalyst. It can be seen that initial slopes of the curves increase greatly by increasing catalyst loading (TiO_2) from 0.25 to 1 g/L for petroleum industry wastewater, thereafter a decrease is appropriate after the same irradiation times. The photo-catalytic destruction of other organic pollutants has also exhibited the same dependency on catalyst dose[8]. This can be explained on the basis that optimum catalyst loading is found to be dependent on initial solute concentration because with the increase in catalyst dosage, total active surface area increases, hence availability of more active sites on catalyst surface[9]. At the same time, due to an increase in turbidity of the suspension with high dose of photo-catalyst, there will be decrease in penetration of UV light and hence photo-activated volume of suspension decreases[10]. Thus it can be concluded that higher dose of catalyst may not be useful both in view of aggregation as well as reduced irradiation field due to light scattering. Therefore the catalyst doses 1 g/L of TiO_2 were fixed for further studies.

Effect of pH :

pH has important influence on pollutant molecules, catalyst surface charge, and also on the mechanism. Wastewater is discharged at different pH. In order to study the effect of pH on the degradation efficiency, experiments were carried out at various pH values, ranging from 2 to 11 for the catalyst loading 1 g/L TiO_2. The pH of each of sample was adjusted at different value using 1 *N* of sulfuric acid or sodium hydroxide solutions. Fig. 3 shows the degradation efficiency of petroleum industry wastewater

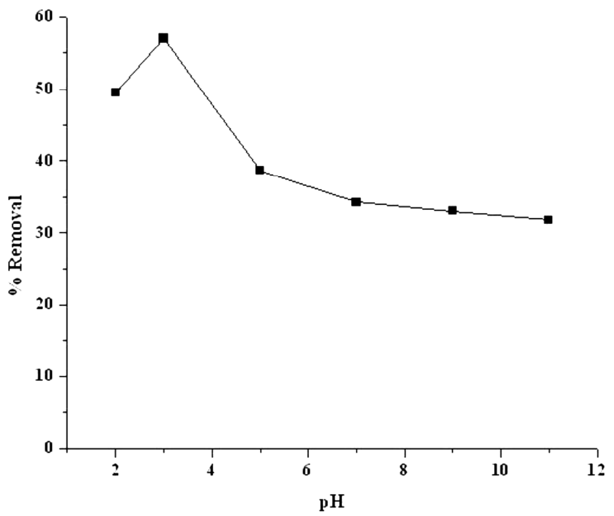

Fig. 3. Effect of pH on degradation of wastewater at (TiO_2 dose – 1 g/L).

as a function of pH. It has been observed that the degradation efficiency initially increases with increases in pH then decrease with increases in pH, exhibiting maximum rate of degradation at pH 3 in case of catalyst loading (1 g/L TiO_2).

Effect of temperature :

The effect of temperature was tested by adjusting the temperatures petroleum industry wastewater samples at different temperatures in the range of 25–50 °C. Fig. 4 shows the removal of organic compounds in the petro-

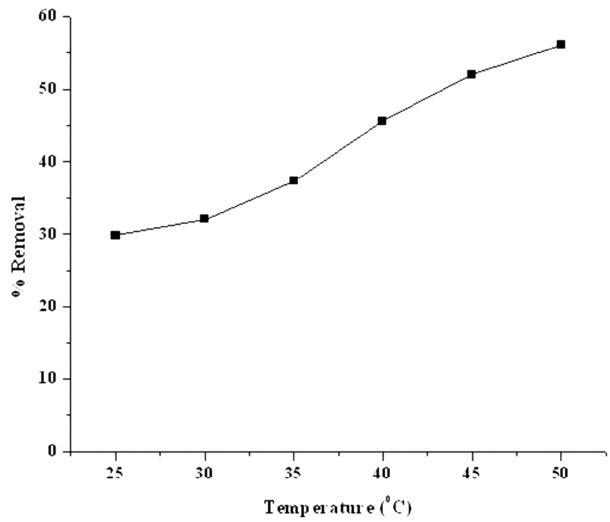

Fig. 4. Effect of temperature on degradation of wastewater at (TiO_2 dose – 1 g/L, pH 3).

leum industry wastewater for experiments conducted at different temperatures. Increase of temperature from 20 to 50 °C has reduced the required time for the pollutants removal. The degradation is favored for most cases by increasing temperature. The reason is related to the TiO_2 electron transfers in valance bond to higher energy levels and hence facilitating the electron hole production. The recombination of electron hole on the surface of photocatalysts will be also promoted by temperature enhancement; however, logically, this promotion will be less extensive when density of the electron holes is high due to high TiO_2 dosage and effective irradiation. Meanwhile, temperature reduces the oxygen solubility in water which is not desirable. On the other hand, increasing temperature causes a global reaction improvement, according to the Arrhenius equation, but an entropy increase and a less adsorption tendency into the catalyst surface is also occurred for the organic molecules. Overall, a positive influence is provided with temperature rise, within the used range. Results showed according to the above mentioned process parameters, the optimum catalyst concentration, pH, and temperature of the solution, for the highest removal, are 1 g/L, 3 and 50 ºC, respectively.

Conclusion

Operating process variables, such as catalyst concentration, pH, and temperature significantly affect the photoactivated process. Results indicated that the degradation of petroleum industry wastewater is facilitated in the presence of catalyst. A very low amount of catalyst such as 1 g/L under pH of 3 and temperature of 50 ºC can be introduced as the optimum operating conditions. Under these conditions, a degradation efficiency of near about 60% of the organic pollutants, determined with COD criterion. The photo-catalytic activity of semiconductors has clearly indicated that TiO_2 as an effective photocatalyst for the removal of organic pollutants in petroleum industry wastewater. Besides higher efficiency, the other advantage of TiO_2 is its low cost than other commercialized catalyst.

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