



Treatment of Oily Wastewater Using Advanced Solar Photo-Catalytic Oxidation Process Using Titanium Dioxide Doped Nano Fibers

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Abstract

General strategy of this study was based on the operational parameters influencing the photo-catalytic degradation rate of oil polluted wastewater treatment. Titanium Dioxide doped nanofibers (TiO₂NFs) with different parameters that affect the photo-catalytic degradation process for oily wastewater were investigated. These parameters are initial oil concentration, catalyst loading and pH. Emulsifier was used in all experiments to increase the solubility of oil in water. Maximum oil removal (81.8%) and (66.2%) decrease in COD was found when the oil initial concentration is 800 ppm, 0.5 g of TiO₂NFs at 180 minutes irradiation time using solar photo-catalytic oxidation technique. Small size of TiO₂NFs particles and its high specific surface and surface energy result in the catalyst agglomeration during the reaction. It causes the reduction of specific surface and limits the multiple application of (TiO₂NFs). It is concluded that nanofibers remarkably enhanced TiO₂ (without doping) catalyst activity in the removal of oil by solar photo-catalytic oxidation. Since, nanofiber is highly adsorptive, this enhanced activity could be relieved to the adsorption of nanofiber. Suitable adsorption capacity is crucial for high photo-catalytic activity. Moreover, the process should be improved in the field of catalyst photo-activity range or the possibility of integration into photo-catalytic reactors.

Keyword: Titanium Dioxide, Doping, photo-catalysis oxidation, Advanced Oxidation Process, Oily Wastewater, Emulsion, oil removal rate.

1. Introduction

Recently, oily wastewater forming an emulsion has greatly increased in machine and tool works and other sources, such as the automotive, aerospace, packing off-shore platforms and mechanical engineering sectors. It is required to clean up effluent water before discharging it to the environment. Oily wastewater in [1] industry can exist in several forms: The emulsified oil is the most difficult to treat [2]. An oil-water emulsion is a colloidal dispersion. These emulsions cannot be discharged in waterways without serious ecological consequences: they impart high chemical oxygen demand, odor, and turbidity [3].

These emulsions typically contain from 100 to 1000 ppm of oil with drop diameter from 0.1 to 10 μm, while the permissible limit for oils and greases in waste water discharged in open water streams is 10 ppm. Therefore it becomes essential to remove oil from wastewater before discharging to final disposal [4].

Oily emulsions can be broken and skimmed off by conventional techniques such as, chemical coagulation, adsorption and biochemical treatment. However, these methods need long settling time, huge land space, and they involve severe sludge handling problems [5]. According to the quality of natural water and clean water deficiency the

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development of cheap waste water treatment and technologies are required. Classical (coagulation/flocculation/ sedimentation, filtration, activated carbon adsorption and chlorination) applied as single or integrated processes are not able to eliminate microorganisms and toxic inorganic and organic compounds from drinking water sources. Thus, the development of novel wastewater treatment processes such as membrane technologies, UV disinfection and Advanced Oxidation Processes (AOPs) is observed. However, those methods enable only the concentration or transportation of impurities to another phase, while their total elimination or neutralizations not obtained. Chlorination is generally applied to cancerogenic products [6].

Advanced oxidation process has widely applications in industry to remove contaminants, such as: cooling towers, Pollutants (COD-BOD) reduction, Drinking water, Waste water industry, Building services, Marine. Advanced oxidation process (AOPs) have emerged as alternative to classical wastewater treatment methods which are environmentally friendly, producing harmless end-products such as CO_2 and H_2O_2 . APOs are in-situ treatment processes characterized by the generation of highly reactive intermediates (OH radicals) which can oxidize the target organic pollutants. Hydroxyl radical is an extremely powerful oxidant nearly as powerful as fluorine and is considerably stronger than H_2O_2 and O_3 [7-11]. There two types of AOPs are homogenous and heterogeneous catalysis which may be included by the UV light to enhance the reaction. This UV light may be sourced from natural sun light or from simulated artificial lamp source. Heterogeneous photo-catalysis is a technology based on the irradiation of the catalyst, usually a semiconductor, which may be photo-excited to form electron-donor sites (reducing sites) and electron-acceptors sites (oxidizing sites), providing great scope as redox reagents.

In this technique, upon radiation with UV, photons from are absorbed by TiO_2 and the electrons on the surface of TiO_2 the electrons and holes can either recombine and produce thermal energy or react with other molecules. The positive holes react with the electron donor (OH^- or H_2O) in the solution to produce OH radical (OH^\bullet), which oxidize the organic compounds on the surface. The holes can oxidize the organic target by direct electron transfer [12]. AOP are based on transient of highly reactive oxidants and

radicals (mainly OH^\bullet , $\text{O}_2^{\bullet-}$, H_2O_2 , O_3) which cause mineralization of organic compounds. Among heterogenic photo-catalysts applied in AOP semi-conductive materials (TiO_2 , ZnO , Fe_2O_3 , CdS , GaP and ZnS) are very popular. Titanium dioxide (TiO_2) is the famous one usually used in photo-catalysis technology. TiO_2 properties with high chemical, physical and thermal stability.

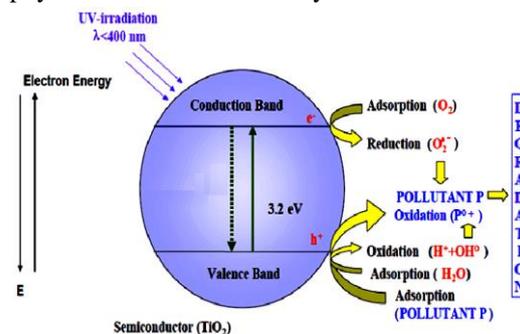


Figure 1: General Mechanism of the Semiconductor Photo-Catalysis Process.

Small size of TiO_2 particles and its high specific surface and surface energy result in the catalyst agglomeration during the reaction. It causes the reduction of specific surface and limits the multiple application of TiO_2 . Moreover, the process should be improved in the field of catalysts photo-activity range or the possibility of integration into photo-catalytic reactors. The treatment of water is focused on mineralization of harmful and chemically and biologically stable contaminants and microorganisms inactivation [13-15]. Photo-catalysis definition and mechanism. These oxygen forms are responsible for oxidation and reduction of compounds adsorbed on catalyst surface. By definition, catalysts takes part in the reaction and speeds transformation of organic compounds, but remains in unchanged form at the end of the catalytic cycle [16]. The aim of the heterogenic photo-catalysis with the use of semi-conductive catalyst TiO_2 is to perform series of redox reactions on the catalyst surface [17-30].

2. Experimental

2.1. Materials

Materials used in this study are: fresh water, emulsifier, engine oil (API SL), sodium chloride (99.9% salt), sodium hydroxide 99%, H_2O_2 solution (35% w/w), H_2SO_4 and hydrochloric acid 30%.

2.2. Photo- Catalyst

Titanium dioxide has attracted great interest in the last decade [17-23]. Non-metal titanium dioxide doping has demonstrated high promise in achieving the performance of titanium dioxide in visible light, with the most powerful dopant being nitrogen. Cation or anion doping is a way to decrease band gap of photo-catalyst in the range of visible light by doping photo-catalyst with transition metals such as ZnS doped with Cu or Ni [24-27], C- doped TiO₂[28] and Ag, Zn and Cd -doped TiO₂ Nano-fibers (NFs) and nano-particles [29]. This way don't decrease band gap only but decrease the recombination time between electrons and holes [30].

2.2.1. Preparation of the Titanium-Doped NFs

A stock solution from the PVP is achieved by dissolving 2g of PVP in 12 ml of absolute Ethanol. To make Titanium Iso-propoxide solution add 2 ml (TTIP) to 4 ml Absolute ethanol and 4 ml Acetic acid and then stir until the solution becomes homogenous. For preparing thiourea doping percent as 0.5%, 0.1%,0.07, 0.05%, and 0.01%; we take 0.764g, 0.1527g, 0.1066g, 0.0764g, and 0.0152g thiourea, respectively and add to it 2 ml ethanol and stir for about 1h and use heater if necessary, to make a clear solution. Make dimethylsulphoxide doping as 0.5%, 0.1%,0.05% and0.01%take 0.686g, 0.137g, 0.0686g and 0.0137g, respectively and add to it 2 ml ethanol and stir for about 1h and use heater if necessary to make a clear solution. Make sodium di-hydrogen orthophosphate doping as 0.5%, 0.1%,0.05% and 0.01% take 1.25g, 0.24g, 0.125g and 0.024g, respectively and add to it 2 ml ethanol and stir for about 1h and use heater if necessary to make a clear solution. Add the stock sol. of the PVP to the desired concentration of thioureasolution, dimethylsulphoxide sol. and sodium di-hydrogen orthophosphate sol. and then continuous stir for at least 1 hour. Finally, dried the fiber sheet for 24h at 60°C, then calcinating the product at 700°C for 5h. Dissolve PVP polymer in ethanol and prepare of doped solutions.

2.3. Experimental Setup

An experimental set-up diagram is shown in

Figure 2. The main part is the parabolic solar reactor is photographed. The solar reactor composed of a UV transparent glass tube (1.5 m long and 40 mm in diameter) connected to a feed tank in a closed recirculation loop with a constant flow estimated to be (60 l/h), which was maintained constant by using a peristaltic pump.

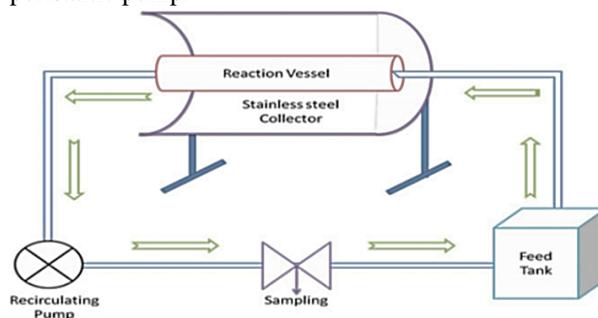


Figure 2: Schematic Diagram of the Solar Photocatalytic Oxidation Unit.

A glass tube from the quartz type is used as a reaction and is mounted in the focal point of the parabolic reflector. An irradiated surface area of 2.1 m² was fabricated from quartz glass sheet placed on fixed metal support as a parabolic concentrating collector that is to be oriented about a horizontal east–west axis so as to constantly minimize the angle of incidence and thus maximize the incident solar intensity.

2.4 Procedure

The solar intensity (J) was found to be approximately constant during the experiments. A stable synthetic emulsion was made to simulate the actual oil emulsions present in practice using fresh engine oil. Each experimental run was carried out in plastic(feed tank) filled with 3l volume of oily wastewater with definite oil solution concentration. A definite dose of the TiO₂-doped nano-fibers (TiO₂NFs) was added to the feed tank with strong mixing. The mixture was re-circulated through the solar reactor tube at a constant flow (1 l/min) for a definite irradiation time. Samples (each of 2 ml) of the oil solution were withdrawn at regular time intervals through the sample valve.

The removal of oil was demonstrated with the decrease in turbidity of the oily wastewater. Dilutions of concentrated samples of oil solution with a begging concentration 1000ppm is used (1000 ppm to 100ppm) and measure the turbidity of each sample. The calibration curve for oil was prepared by

recording the turbidity values for a range of known concentrations of oil solution in Figure 3.

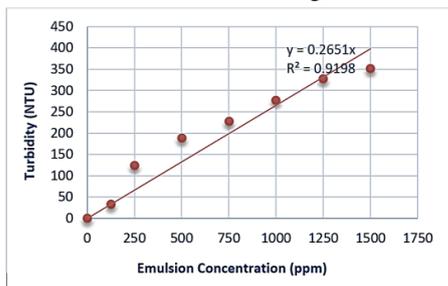


Figure 3: Dilution Calibration Curve of Oil

2.5. Catalyst Characterization for Prepared Nano Fibers

X-ray diffractometer (XRD) described the phase and crystallinity of the catalyst nanofibers; (TEM) and (EDX) tests are commonly used to validate the percentage and atomic ratio of components for the study of catalyst nanofibers and (SEM)[31-32]. Structure analysis of the pure TiO_2 in Figure 4 exhibited characteristic anatase phase pattern (JCPDS 89-4921), with diffraction peaks at 2 theta values of 25.4° , 37.8° , 48.2° , 53.9° , 55.2° , 62.8° , 69.0° , 70.5° and 75.2° , these results is in good agreement with [41]. The XRD patterns of calcinated TiO_2 fibers is presented in Figure 4. It indicates sharp and well-defined peaks, suggesting the crystalline of the synthesized materials.

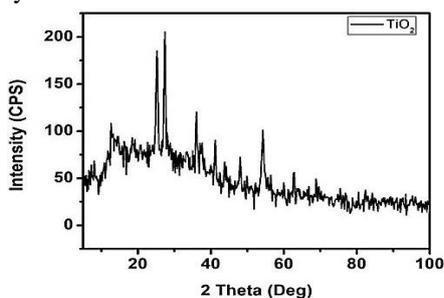


Figure 4: XRD Patterns for TiO_2 Nanofiber.

Diffractograms of N-doped TiO_2 nano composites showed in Figure 5 very similar pattern to anatase, without additional peaks. On the other hand, even though the diffractograms corresponding to N-doped TiO_2 nano- composites showed similar pattern to pure TiO_2 , additional peaks at 21.6° and 24° were observed. These reflection peaks corresponded to a typical orthorhombic unit cell structure of (110) and (200) reflection planes respectively, corresponding to

N-doped TiO_2 [33].

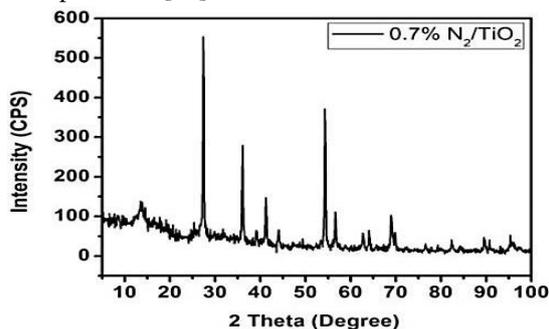


Figure 5: XRD Patterns for 0.07% N-Doped TiO_2 Nano-fibres.

The XRD patterns in Figure 6 demonstrate that the phosphorus-doped titanium contains only the anatase phase above the $400\text{--}700^\circ\text{C}$ calcination level. Thus, we assume that the phosphorus alteration effectively prevents the anatase to rutile phase change.

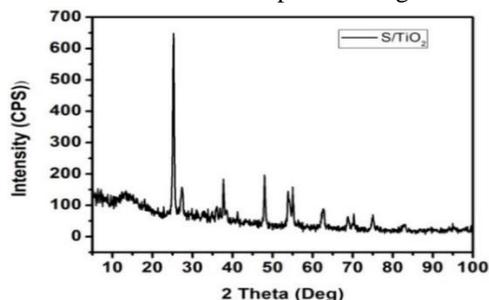


Figure 6: XRD Patterns for S-Doped TiO_2 Nanofibers.

Notably, the peak corresponding to the (101) plane for TiO_2 and P- TiO_2 is located at 25.37° and 25.49° , respectively. The slight shift of the (101) plane of P- TiO_2 likely implies that the P element should be doped into the crystal lattice of anatase. The XRD patterns in Figure 7 demonstrate that the phosphorus-doped titanium contains only the anatase phase above the $400\text{--}700^\circ\text{C}$ calcination level. Thus, we assume that the phosphorus alteration effectively prevents the anatase to rutile phase change. The morphologies of as-synthesized and calcined un-doped TiO_2 NF are seen in SEM images in Figure 8.

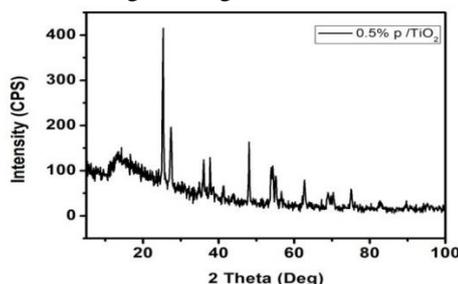


Figure 7: XRD Patterns for P- Doped TiO₂ NFs.

3. RESULTS AND DISCUSSION

3.1. Evaluation of TiO₂ NFs Performance

The enhancement of TiO₂NFs was achieved by using TiO₂ doping nanofibers. Increased adsorption leads to higher concentration of oil around TiO₂. This exhibits synergism, in which the adsorbed oil molecules on the nanofibers are transferred to TiO₂ where they are degraded under solar irradiation.

A comparison between naked TiO₂ without doping and TiO₂ at the same operating conditions on the removal of oil by solar photo-catalytic oxidation is shown in Figure 9. It was noticed that the photo-catalytic activity of TiO₂ improved using the prepared photo-catalyst TiO₂NFs. The prepared TiO₂, exhibited higher photo-catalytic activity under sunlight. The prepared photo-catalyst was stable after the removal of oil by solar photo-catalytic oxidation.

Suitable adsorption capacity is crucial for high photo-catalytic activity. An important step in the photo-catalytic process is the adsorption of reacting substances onto the surface of the catalyst [35-38]. The higher oil removal efficiency in this case was attributed to the particle size and high surface area of the prepared photo-catalyst.

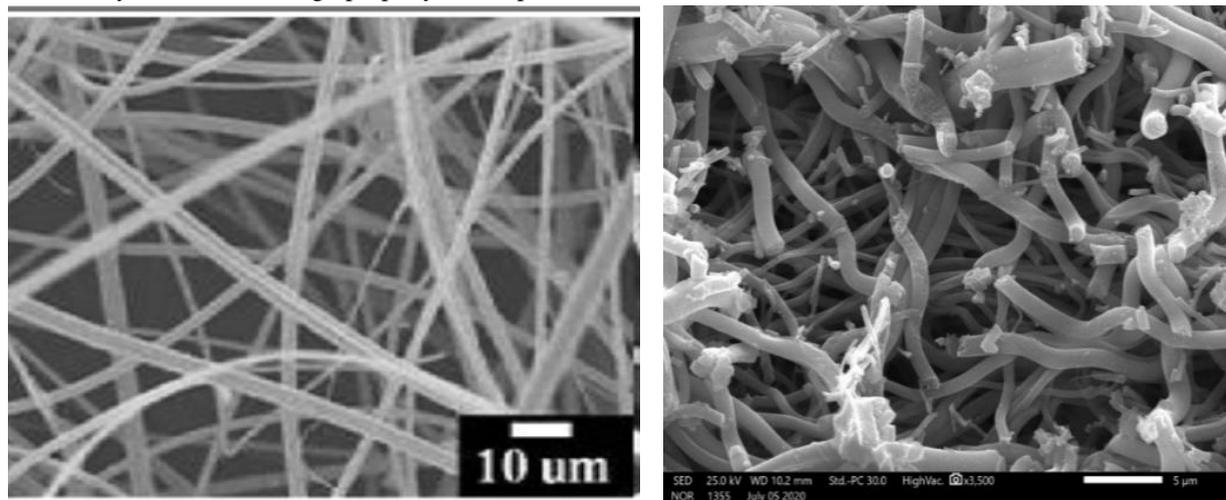
3.2. Effect of pH

The photo-catalytic degradation efficiency is affected by the surface charge property of the photo-

catalyst, charge of the molecule, adsorption of molecule onto photo-catalyst surface and hydroxyl radical concentration. pH dependent, it plays an important role that influences on the degradation of pollutants.

From the experimental results shown in Figure 10, the efficiency of oil removal using solar photo-catalytic oxidation over TiO₂/TiO₂NFs is increased up to pH equal 8. Hence the higher oil removal efficiency is due to the strong adsorption of oil on the catalyst surface.

The maximum oil removal reaches 81.8% within 180 minutes irradiation time and with a dose of photo-catalyst equals 0.5 g/l. The photo-catalytic activity of TiO₂/ TiO₂NFs was strongly influenced by the pH of the reaction solution due to its amphoteric behavior. At low pH, corrosion of TiO₂/ TiO₂NFs occurred and photo-catalytic reaction is prohibited due to dissolution of TiO₂/ TiO₂NFs in the solution as well as decreasing adsorption of the oil over the photo-catalyst. This leads to lowering of oil removal efficiency. At higher pH over 8, the oil removal efficiency started to be decreased, this attributed with the presence of groups in its structure, which is negatively charged in alkaline conditions (pH > 9). Therefore, effective oil removal is hindered from electrostatic reasons. Hence, at intermediate pH, i.e. between 7 and 8 optimum conditions for oil removal by solar photo-catalytic oxidation with hydroxyl radicals.

Figure 8: SEM Image for TiO₂ NFs before Doping

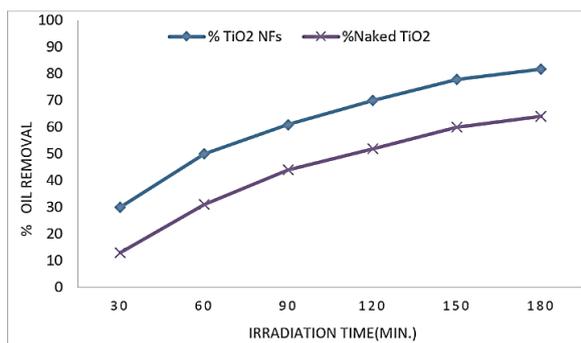


Figure 9: Comparison between Naked TiO₂ and TiO₂NFs on Oil Removal by Solar Photo-Catalytic Oxidation [TiO₂ 0.5 g/l, pH = 7, Oil Concentration 800 mg/l]

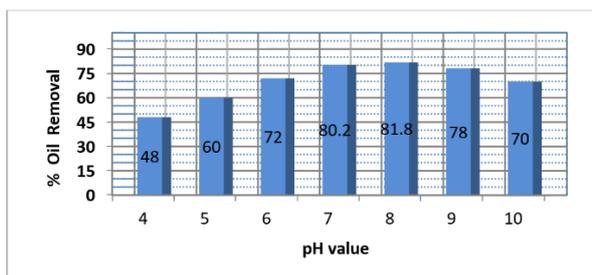


Figure 10: Oil Removal % vs. pH Values by Solar Photo-Catalytic Oxidation [TiO₂NFs dose 0.5 g/l, Oil Concentration 800 mg/l, Solar Irradiation Time = 180 min.]

3.3. Effect of Oil Concentration

The effect of oil concentrations was investigated in the range 800, 1000 and 1200 mg/l and the results are illustrated in Figure 11. It was found that the increase in oil concentration decreased the removal rate of oil. When the oil concentration is increased from 800 to 1200 mg/l, the decrease of the oil removal from 81.8% to 68.3% and decrease of the COD removal from 65% to 27% were achieved within 180 min. of irradiation.

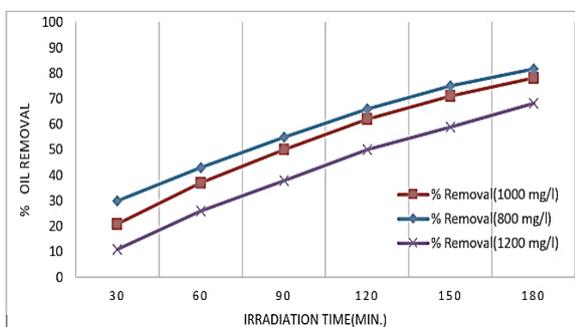


Figure 11: Effect of Oil Removal by Solar Photo-catalytic Oxidation [TiO₂NFs Dose 0.5 g/l, pH = 7 and Solar Irradiation Time = 180 min]

As initial concentration increases, more and more oil is adsorbed on the surface of TiO₂NFs photo-catalyst. This reduces the generation of hydroxyl radicals, since there are only a few active sites for the adsorption of hydroxyl ions and the generation of hydroxyl radicals. Further, as the concentration of oil solution increases, incident photons were adsorbed by oil before they can reach the catalyst surface. Hence, the absorption of photons by the catalyst decreases, and consequently the degradation rate of oil is reduced [39-41].

3.4. Effect of Catalyst Dose

The amount of semiconductor as catalyst is one of the main parameters for the heterogeneous photo-catalytic oxidation studies. The effect of catalyst loading on degradation of the oil removal over TiO₂NFs is shown in Figure 12 using visible solar light. The catalyst loading changed from 0.25 to 1 g/l on 0.25 intervals. The Figure shows that the % removal of oil was enhanced when the amount of catalyst in the reactor increased up 0.5 g/l over TiO₂NFs and then decreased. It should be pointed out that, the catalyst loading affects number of active sites on the photo-catalyst and the penetration of radiation through the suspension. As the catalyst loading increases the % removal of oil decreases due to the enhancement of light reflectance by nano fiber. The number of active sites increases but the penetration of radiation decreases due to shielding effect [42-45]. Solar photo-catalytic oxidation, which is influenced by both the number of active sites and the penetration of irradiation light, must therefore pass through a maximum at optimum catalyst loading. Also, the decrease in adsorption density with increase in adsorbent amount is due to the high number of unsaturated adsorption sites [46-49].

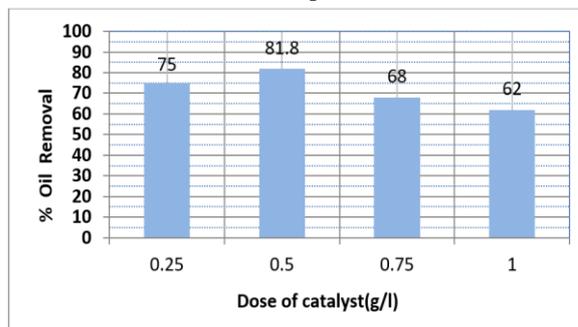


Figure 12: Effect of Catalyst Load on Oil Removal by Solar Photo-Catalytic Oxidation [Oil Concentration = 800 mg/l, pH = 7 and Solar Irradiation Time = 180 min]

It should also be noted that the optimum value of catalyst loading is strongly dependent on the type and initial concentration of oil and the operating conditions of the solar photo-reactor [46-50]. In our study, the optimum catalyst loadings of TiO₂NFs is 0.5 g/l. Corresponding oil removal was 81.8% within 180 min irradiation time and pH= 7.

3.5. Photo-Degradability

Figure 13 shows the results of photo-degradation of oil with TiO₂NFs under solar light under different doses of catalyst. In the absence of photo-catalyst the oil removal, on irradiation with the solar light alone, has been found to be nearly stable. In the presence of 0.25 g/l TiO₂NFs about a 40% only of COD removal was observed within 180 min solar irradiation time. This is due to the adsorption of the oil present in the wastewater on the surface of TiO₂NFs at pH = 7. The maximum COD removal with 66.8% is achieved at 0.5 g/l of TiO₂NFs at pH=7 and initial oil concentration 800 mg/l within 180 min. irradiation time. As shown from the Figure 13 the changes of COD removal in the reaction solution during the solar photo-catalytic oxidation process of the oily wastewater at different catalyst loading are exhibited.

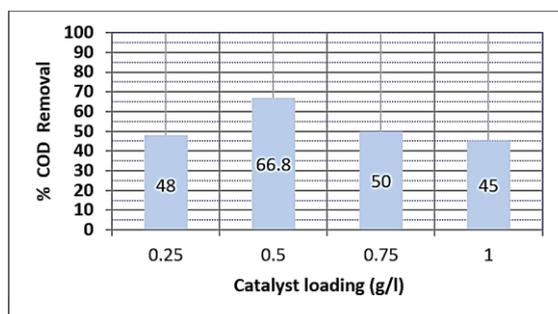


Figure 13: Effect of catalyst loading on COD removal by solar photo-catalytic oxidation [Oil concentration = 800 mg/l, pH = 7 and solar irradiation time = 180 min]

As indicated, the COD removal is increased with the increase of the dose of the prepared photo-catalyst within 180 irradiation time and pH = 7 using initial oil concentration of 800 mg/L. The % COD removal then increased with time but very slowly till a constant dose of photo-catalyst. Behind a value of 0.5 g/l of catalyst, the % of COD is decreased. These results indicate that the fast oil removal was followed by much slower mineralization of intermediates formed subsequently. On the other hand, the persistence of a low but constant COD removal in

solution suggests the accumulation of dead-end products which are resistant to the degradation by the solar photo-catalytic oxidation reaction. Therefore, it should be readily removed by biological treatment systems and is unlikely to pose a problem to the environment [48-49].

4. Conclusion

TiO₂NFs photo-catalyst was prepared by facile method to avoid the problem of photo-catalyst recovery.

The solar photo-catalytic activity for oil removal from oily wastewater over TiO₂NFs prepared photo-catalyst was investigated. The TEM results showed smaller particle sizes of TiO₂NFs. Additionally, TiO₂NFs showed higher photo-catalytic activities for oil removal than naked TiO₂.

It was observed that oil removal and COD removal with 81.8 % and 66.2 % respectively were achieved within 180 min. irradiation.

The results are worth noting that efficient oil removal using solar photo-catalytic oxidation was favorable in neutral and alkaline media (pH = 7 to 9).

The higher oil removal value in this case was ascribed to the smaller particle sizes and high surface areas of the prepared photo-catalyst.

Additionally, there was a significant increase in the band-gap energy along with a decrease in the particle size of TiO₂NFs composite.

Therefore, TiO₂NFs is promising solar light active materials for photo-catalytic degradation and mineralization of oils containing wastewater.

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