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Treatment of Industrial Wastewater by Solar Nano Photocatalysis

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Abstract: Experimental investigations were carried out to find environmental friendly and effective solution by harnessing of solar energy through photocatalysis to degrade the contaminants present in wastewater using ZnO nano particles as photocatalyst. Multilayer thin film of photocatalyst (ZnO) was developed inside the glass tube reactor by layer-by-layer (L-b-L) method. Effluent samples were collected from four industries in the sultanate of Oman and a series of experiments were carried out in a ZnO thin film coated reactor under solar radiation exposure for 4 hours. pH, COD, TOC , TDS and Turbidity was analyzed for the samples collected on hourly basis and a comparison of treatment showed substantial degradation of pollutants in all the wastewater samples and also complete de-colorization of sewage wastewater.
Keywords: Wastewater; Solar Photocatalysis; Total organic carbon; Zinc oxide.

Introduction

The contamination of water sources and pollutants of chemical compounds arising from the discharge of wastewater from the chemical industries, power plants, landfills, and agricultural fertilizers remains the issue of a global concern. The existence of such pollutants represents a technical challenge in conventional water treatment processes and the most difficulties faced are the removal of trace contaminants and toxic compounds. This technical shortage in the treatment of trace contaminants, has led to growing public concern from environmental point of view and the need to develop modern techniques with low cost [1, 2, 3]. Photocatalysis is an advanced oxidation technology that uses the catalytic activity of the semiconducting metal oxides. This technology produces $OH^{\cdot}$, which has stronger oxidation power than ordinary oxidants normally used in the oxidation process, and decomposes the organic compounds into harmless compounds, such as CO_2, H_2O, or HCl [4]. Many types of semiconductors have been used as photocatalyst including TiO_2, ZnO, CdS, WO_3, etc. Most of these semiconductor photocatalysts have band gap in the ultraviolet (UV) region, equivalent to or larger than 3.2eV (λ = 387 nm). When photocatalyst absorbs Ultraviolet (UV) radiation from sunlight or illuminated light source, it will produce pairs of electrons and holes. The excess energy of this excited electron promoted the electron to the conduction band therefore creating the negative-electron (e^-) and positive-hole (h^+) pair. This stage is referred as the semiconductor's 'photo-excitation' state. The energy difference between the valence band and the conduction band is known as the 'Band Gap'. The positive-hole of photocatalyst breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. The activation of ZnO by UV light can be represented by the following steps [5, 6].

$$ZnO + h_v \longrightarrow e^- + h^+ \quad (1)$$
$$e^- + O_2 \longrightarrow O_2^{\cdot -} \quad (2)$$
$$h^+ + \text{Organic} \longrightarrow CO_2 \quad (3)$$
$$h^+ + H_2O \longrightarrow {}^{\cdot}OH + H^+ \quad (4)$$
$$OH + \text{Organic} \longrightarrow CO_2 \quad (5)$$

The Layer-by-Layer coating method is one of the simple and low-cost techniques for preparing thin films on supported materials such as glass plates; steel fibers; perlite granules and aluminum foil [7,8,9]. In the present experimental studies, the L-b-L method was used for catalyst coating inside the glass tubes and then a recirculation reactor set up was fabricated using a peristaltic pump. The main aim of the study was to investigate the effectiveness of using ZnO nanoparticles thin film for the treatment of different selected Oman industrial wastewater by harnessing solar energy in an efficient and environmental friendly way [10, 11].

Materials and Methods

Chemicals and Analysis

All chemicals were purchased from standard organization. The photocatalyst ZnO nano powder (99.9%, APS: 20 nm) was obtained from mkNANO, Chitosan (CAS: 9012-76-4) from Molekula, and Acetic acid (100%) from Mervick. 0.1 N NaOH and 0.1 N HCl are used for pH adjustment. Distilled water was used throughout for all experiments. Shimadzu, Japan make saline water total carbon analyzer was used for TOC analysis of the samples. The COD was analyzed by using the Chemetrics Analyzer and TDS, pH were analyzed by Eutech make water analysis kit.

Samples collection

Wastewater samples were collected from four different industries in Oman, they are: (1) ORPIC, the wastewater sample was collected from the final unit after separation of oil. (2) OMIFCO, the wastewater sample was collected from the final unit. (3) Textile industry wastewater was collected from OTM and pretreated using desert sand column before applying the solar photo catalysis treatment. (4) Al-Khoudh Municipal Wastewater Plant from the secondary treated unit. The samples were transferred and stored immediately under refrigerated condition in the lab. The initial characteristics of collected samples have been shown in table 1.

Table 1: Initial characteristics of collected samples effluent

Parameters	OMIFCO	ORPIC	OTM	Sewage
pH	5.52	8.18	8.71	7.81
TDS (ppm)	2.18	6.65	3.1	2.67
COD (ppm)	380	419	2780	1384
TOC (ppm)	8.82	11.30	119.4	204.1
Turbidity	0.92	0.94	26	57.69

Preparation of photo catalysts coating

The catalyst coating solution was prepared by addition of 2 g of chitosan into 100 ml of 1% acetic acid. The mixture was stirred until the polymer dissolved completely and then, 0.2 g of ZnO catalyst was added to the prepared solution and kept under stirring for 5 hours with constant heating at 60°C. Three Glass tubes with dimension of 0.5m in length and 0.01m inner diameter were coated using Layer-by-Layer (L-b-L) coating process. The prepared polymer solution was poured into the glass tube and allowed to coat for 15 min and the excess solution is rinsed followed by drying using forced hot air. The coating process was repeated for 10 times in order to get proper thin film.

Batch experiment for testing the stability of thin film

Seven glass plates of dimension (0.08×0.03×0.001m) were coated with prepared polymer solutions by dip coating technique and the process was repeated for 10 times. Seven beakers of 100 ml distilled water were prepared using 0.1N NaOH and 0.1N HCl with the help of pH meter to adjust the required pH of 2, 4, 6, 7, 8, 10, 12. The coated glass plates were immersed into the different pH solutions for one day to test the stability of the thin film. By visual observation, it was noticed that the thin film was completely removed at pH of 2 and 4, whereas it was more stable at pH of 7,8,10 and 12.

Solar Photocatalytic Experiments

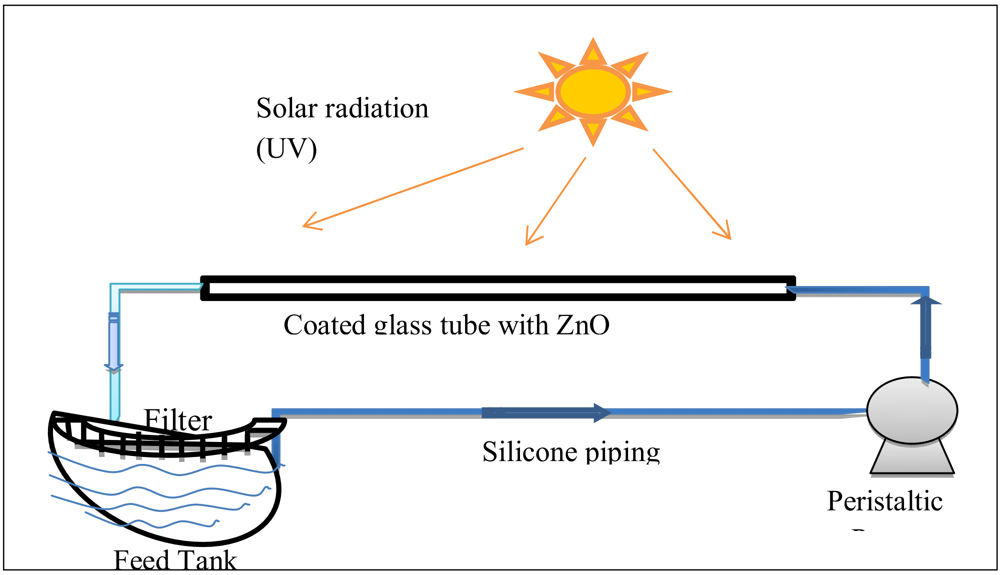

Figure 1. The schematic diagram of the Experimental Set up

The experimental set up consists of the catalyst coated reactor, feed glass tank with capacity of $0.002m^3$ and a peristaltic pump with silicone piping as shown in Figure 1. The experiments were conducted under solar radiation at Caledonian College of Engineering Campus in Oman from 9 AM to 3 PM in the month of March - April of the year 2014. During this period a maximum UV-index of 11 was determined for the solar radiation. Four sets of experiments were carried out with 0.0015 m^3 of the feed wastewater using ZnO coated reactor. The discharge was re-circulated through the reactor system with speed of 85 rpm for a period of 4 hours. The samples were collected every 1 hour and filtered before analyzing for parameters COD, TOC, TDS, DO, pH, and turbidity.

Results and Discussion

pH variation of four wastewater samples exposed to solar radiation for 4 hours in ZnO coated reactor was shown in Figure 2. There is a slight decrease in pH of all wastewaters during the photocatalytic reaction which can be related to the participation of the $OH^{\cdot}$ radicals in oxidizing the pollutants and leaving the H^+ in the sample which leads to decrease in the alkalinity of the treated samples.

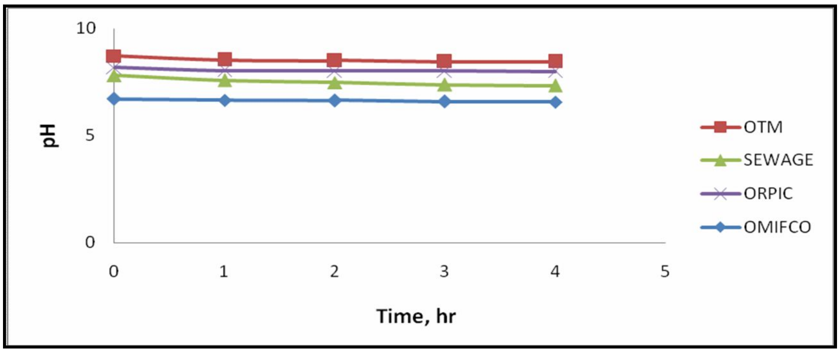

Figure 2. Variation of pH with respective to solar photocatalysis reaction time

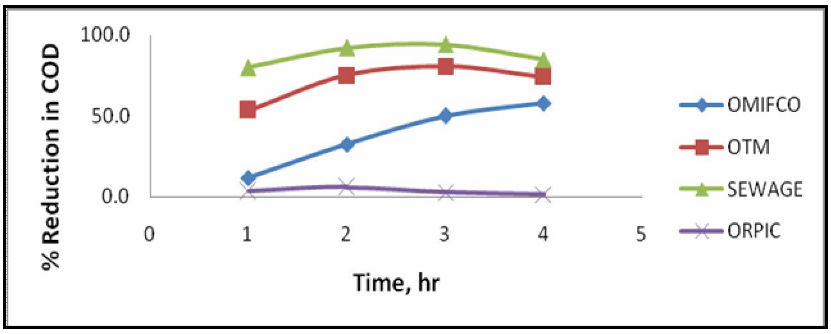

Figure 3. % Reduction of COD with respective to solar photocatalysis reaction time

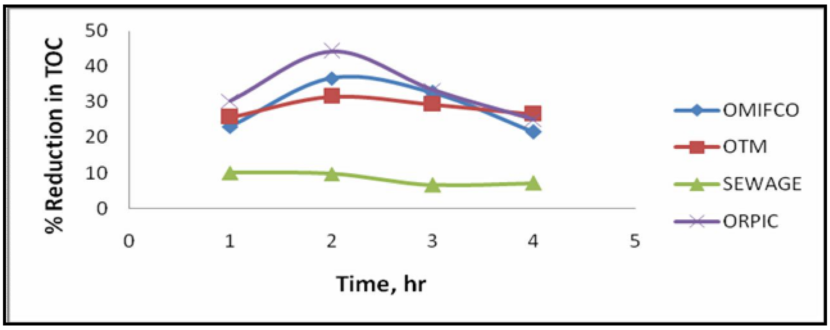

Figure 4. % Reduction of TOC with respective to solar photocatalysis reaction time

The effects of degradation of COD and TOC with respective to time are shown in Figure 3 and 4 respectively. The major reduction of COD is achieved for sewage sample where it reaches to 94% within 3 hours of exposure to sunlight whereas the wastewater of OTM. OMIFCO and ORPIC reached 75%, 60% and 6% reduction respectively. The maximum reduction of TOC was achieved within two hours of exposure to the solar radiation. ORPIC wastewater achieved the highest percentage of reduction i.e. 44% followed by OMIFCO wastewater sample with 37%, OTM with 30% and sewage wastewater with 10% of reduction in TOC respectively. The reduction of COD and TOC is mostly based on the organic pollutants present in the wastewater samples and its potential diffusional rate towards catalyst surface.

The comparisons of TDS reduction for the four wastewater samples are shown in Figure 5. It was observed that there is steady increase in percentage reduction of TDS in municipal sewage and OTM samples whereas in case of OMIFCO and ORPIC samples, it was increased for 2 hours and then decreased, which may be due to formation of more byproducts in later case. A maximum reduction of 7% in sewage sample, 2% in OTM, 20% in OMIFCO and 5% in ORPIC samples was observed. The variation of turbidity for the four wastewater samples was shown in Figure 6.

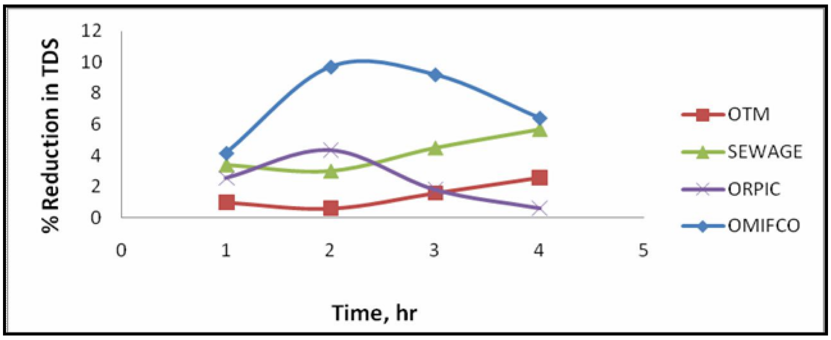

Figure 5. % Reduction of TOC with respective to solar photocatalysis reaction time

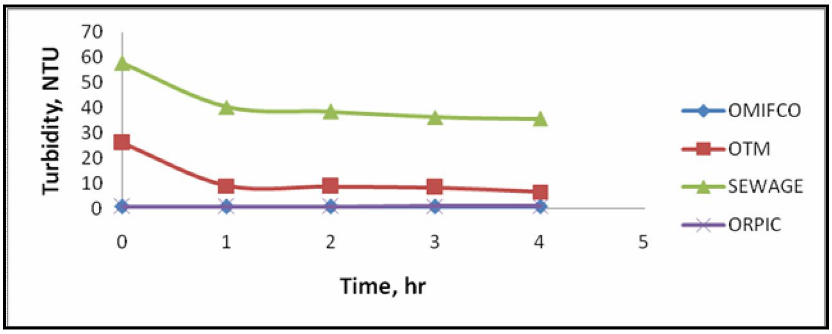

Figure 6. Variation of Turbidity with respective to solar photocatalysis reaction time

There is negligible change in removal of turbidity for OMIFC and ORIPIC samples, this may be due the fact that the samples collected were from the final pretreatment process, which is almost free of turbidity. However an appreciable change in turbidity was observed for sewage and OTM samples. It decreased from 60 NTU to 35 NTU in sewage and 28 NTU to 10 NTU in OTM respectively, and the decrease of color is around 40% in sewage sample which indicates the efficiency of ZnO photo catalyst in removal of color from sewage wastewater sample. Figure 7 shows the color change in sewage wastewater sample.

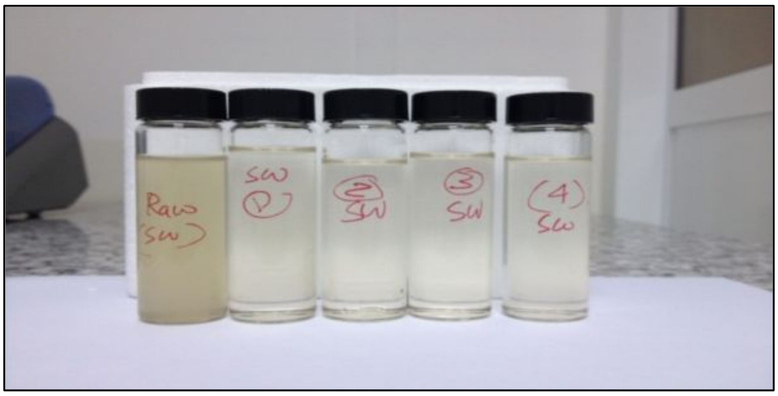

Figure 7. Variation of Color with respective time for Sewage sample

Conclusion

In this present study, the effectiveness of using ZnO nanoparticles by solar photo-catalysis in removing toxic organic pollutants from selected wastewater influents from different industries in Sultanate of Oman was investigated.Multilayer thin film using chitosan polymer was fabricated by L-b-L method in glass tube which used as reactor. The collected samples were treated with ZnO thin film and different parameters were analyzed and found that ZnO photocatalyst has good ability in removing the trace pollutants present in industrial wastewater. The comparison for the treatment of four treated wastewater samples using ZnO thin film showed almost constant pH variation for all samples. A maximum of 10% reduction of TDS in OMIFCO water sample, 94% reduction of COD in sewage water sample and 44% reduction of TOC in ORPIC sample was observed.

Acknowledgment

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