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Photocatalytic Degradation of Produced Water Hydrocarbon of an Oil Field by Using Ag-Doped TiO_2 Nanoparticles

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***Abstract*—**In this study, the removal of pollutants of a real produced water sample from an oil reservoir (a light oil reservoir), using a photocatalytic degradation process in a cylindrical glass reactor, was investigated. Using TiO_2 and Ag-TiO_2 in slurry form, the photocatalytic degradation was studied by measuring the Chemical Oxygen Demand (COD) parameter, qualitative analysis, and GC-MS. At first, optimization of the parameters on photocatalytic degradation of hydrocarbon pollutants in real produced water, using TiO_2 nanoparticles as photocatalysts under UV light, was carried out applying response surface methodology. The results of the design of the experiment showed that the optimum conditions were at a catalyst concentration of 1.14 g/lit and pH of 2.67, and the percentage of COD removal was 72.65%.

***Keywords*—**Photocatalyst, Ag-doped, TiO_2, produced water, nanoparticles.

I. Introduction

THERE is no doubt that oil and gas are central to modern civilization; however, as with most production activities, oil and gas extraction is associated with a significant amount of waste, sometimes referred to as produced water [1]-[4]. Among all the pollutants produced to date, a high level of contamination in the produced water was observed, containing a large number of hydrocarbons in both suspension and solution, toxic inorganic materials, heavy metals, and soluble gases, bringing about significant environmental concerns when discharged offshore and onshore [5]-[8]. Since it is not necessary to inject the produced water into an adjacent reservoir for enhanced oil recovery, the produced water should be treated in accordance with the standard limits of discharge to the environment or the further reuse of it in industries or agricultural purposes [9]-[13].

There are several physical and chemical approaches as well as mixed approaches in order to treat the produced water. During the production process, the wastewater is contaminated by several sources of pollution, one of which is hydrocarbons that can vary depending on the type of generated oil or gas and the reservoir from which the oil or gas is derived. There are numerous methods that can be used to degrade these components efficiently, and one of these methods is photocatalytic oxidation [14]-[17]. It has been demonstrated that despite the existence of numerous photocatalysts, such as TiO_2, ZnO, etc., which have been studied in previous studies, titanium dioxide is the most commonly used for the removal of organic components due to its high photocatalytic activity, non-toxicity, chemical stability, and the fact that it is a reasonably priced catalyst [15]-[18].

It is of so great importance to find an appropriate catalyst that could be used during visible light and solar light illumination under an industrial scale of wastewater treatment due to the high capital costs and the hazards involved with ultraviolet light. With the help of CTAB surfactant, an Ag-TiO_2 and a modified TiO_2 were synthesized and evaluated as visible light active photocatalysts. Furthermore, we examined their performance in comparison to commercial TiO_2 for degradation of hydrocarbon components in a real sample of produced water obtained from the Cheshmeh-Khosh oil reservoir (light oil) in the optimal conditions suggested by the design of the experiment, measuring COD parameters from the effluent of the process.

II. Experimental

A. Materials

Titanium dioxide nanoparticles (P25) with a surface area of 50.4 nm as measured by the Brunauer-Emmett-Teller (BET) method were supplied by Evonik Company. The nanoparticles are composed of 80% anatase and 20% rutile. The chemicals used in the study, including TTIP titanium (IV) isopropoxide, ethanol, ammonium hydroxide (NH_4OH), ammonium thiocyanate (NH_4SCN), and cetyltrimethyl ammonium bromide (CTAB) were sourced from Merck. This is the real produced water of the Cheshme-Khosh oil reservoir (light oil reservoir).

B. Methods

The procedure involved the addition of 4.59 ml of titanium (IV) isopropoxide drop-by-drop to 200 ml of ethanol containing 4.72 gr of ammonium thiocyanate and 1 gr of CTAB under vigorous stirring, resulting in a solution of titanium (IV) isopropoxide. For the second step, 0.62 ml $AgNO_3$ (0.5M) and 1 ml NH4OH were added to the first solution, and it was allowed to stand for 15 minutes. In a binary reactor that was put at 60 °C for an extended period of time, the ethanol-containing final solution was stirred for five minutes at room temperature. In order to prepare the sample, a vacuum oven was filled with the dry sample and kept at 60 °C for one hour before it was calcined to 500 °C in air at a

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heating rate of 5 °C in two hours.

There were two other catalyst samples synthesized in the same conditions without $AgNO_3$ and NH_4SCN, or just without NH_4SCN, respectively for TiO_2 (with CTAB surfactant) and Ag-TiO_2.

According to the Standard Methods, Method Number 5220D, COD was determined following the steps outlined in the procedure [19]. GC-MS was applied to detect all of the hydrocarbon compounds present in produced water, and it was applied to both prototype effluents and output of a photocatalytic process, carrying out the analysis under optimum conditions and with TiO_2 (p-25) catalysts.

C. Characterization

The crystallinity of the synthesized nanoparticles was checked by powder X-ray diffraction (XRD). XRD measurements were performed on an Equinox 3000 X-ray diffractometer (Inel, France) with Cu Kα (λ = 0.15406 nm) radiation from 20◦ to 90◦ in 2θ.

The morphology and the size of TiO_2 nanoparticles were investigated by Field Emission Scanning Electron Microscopy (FESEM) with a JEOL JEM-2010 electron microscope.

D. Photocatalytic Degradation

It must be noted that all the reactions for photocatalytic oxidation took place in a cylindrical double-walled glass vessel, which connected the outer walls of the vessel with the water circulation pump that was capable of maintaining a constant temperature within the vessel.

In order to obtain uniform illumination of the reactor contents of the effluent, a magnetic stirrer was placed over the reactor and a magnet was used to homogeneously stir the contents of the reactor. An air pump and sparger were installed in the reactor in order to ensure that oxygen was evenly distributed throughout the solution, which is necessary for photocatalysis. As a result of the air bubbles, more of the solution's surface area was exposed to oxygen, adding to the reaction's efficiency. In addition to a UV lamp, a visible lamp of 160 W was also installed in the reactor, depending on the experimental requirements. The experiments were performed according to the design of experiments with pH and catalysts concentration as variable parameters, to achieve maximum removal efficiency of COD in the presence of commercial photocatalyst TiO_2 (p-25) to form a slurry and were repeated for synthetic catalysts in optimal conditions (pH = 2.67 to 1.14 gr catalyst concentration l).

III. Results

According to the data from X-ray diffraction analysis, Ag-TiO_2 represented the anatase phase. Figs. 1 and 2 show the XRD patterns of synthesized TiO_2 and Ag-TiO_2 respectively [7]-[10].

Figs. 2 and 3 show the FESEM of nanoparticles that confirm the spherical structure of nanoparticles. Fig. 4 shows the EDX spectra of Ag-TiO_2. It confirmed the presence of Ag with a weight percentage of approximately 4.3%. Additional peaks observed in EDX analysis were associated with Au present in the gold coating deposited on the samples [20].

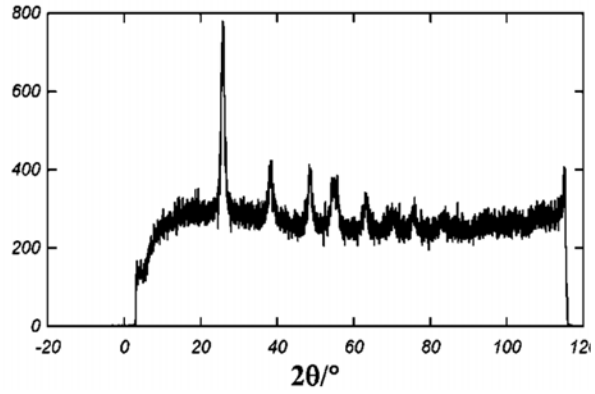

Fig. 1 XRD pattern of TiO_2

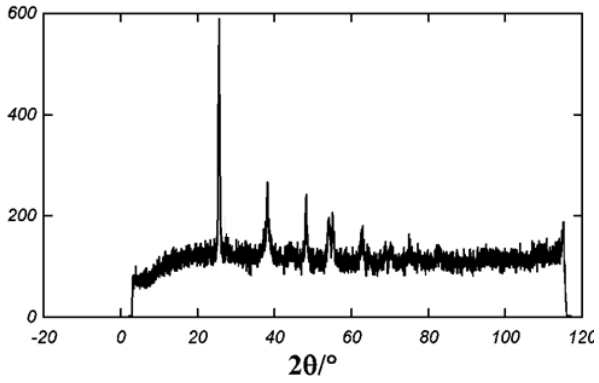

Fig. 2 XRD pattern of Ag-TiO_2

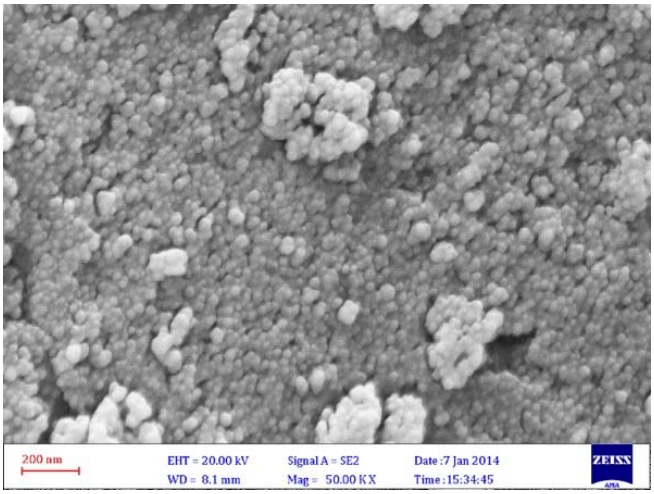

Fig. 3 FE-SEM images of TiO_2

COD reduction observed in the optimum conditions for commercial catalyst TiO_2 (p-25) and the synthesis of TiO_2 using UV irradiation was 72.65% and 68.29% respectively. For Ag-TiO_2 catalysts compared to TiO_2 (p-25) and for the synthesized TiO_2 under visible light, an improved COD removal efficiency of 26% and 30% was observed respectively (Fig. 6). The results of GC-MS analysis, indicate that mostly heavy hydrocarbons were degraded, and were

converted into intermediate materials, completely disappeared or decreased in concentration [20]-[23].

As can be seen from the results of GC-MS analysis of the input to the reactor in Table I, the inlet (produced water) mainly included dibutyl phthalate, squalene and bis(2-ethylhexyl)phthalate at 39,19 and 9%, respectively. However, after photodegradation and breakdown of the chemicals within the input flow, the remaining compounds in the output mainly included squalene, octadecenoic acid, bis(2-ethylhexyl) phthalate and alpha-terpineol at 27, 16, 10 and 9%, respectively. The results well confirm the breakdown of toxic and heavy hydrocarbons into intermediate and light ones.

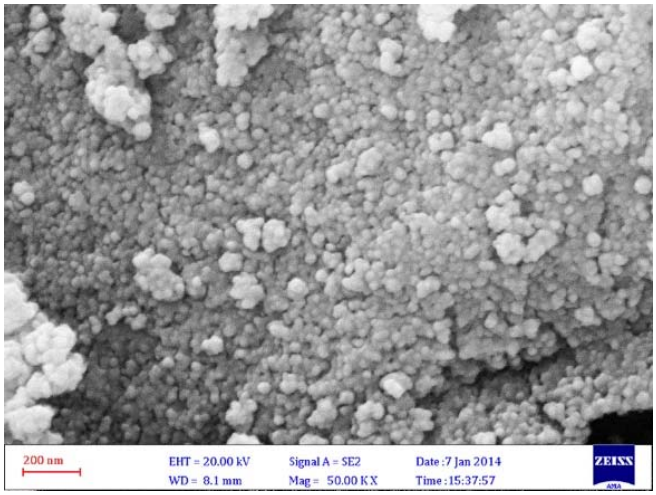

Fig. 4 FE-SEM images of Ag-TiO_2

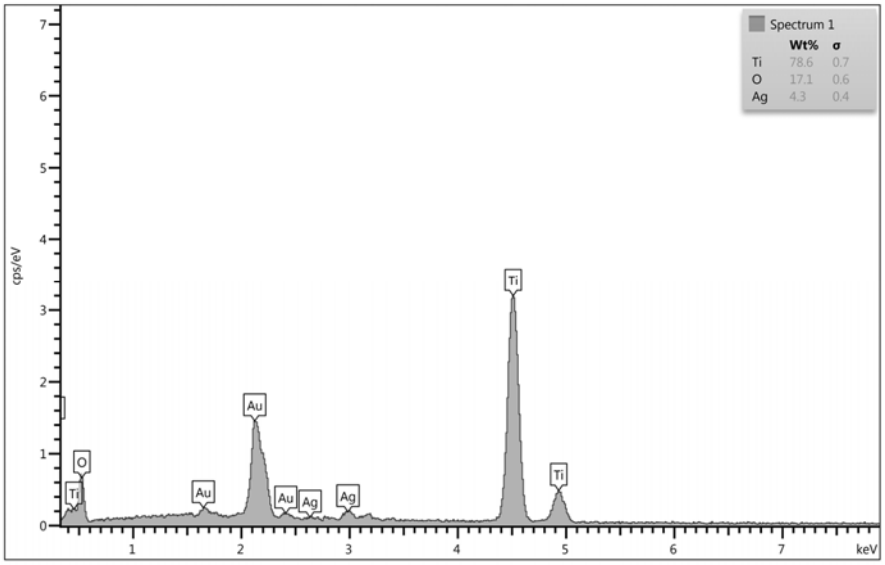

Fig. 5 EDX spectra of Ag-TiO_2

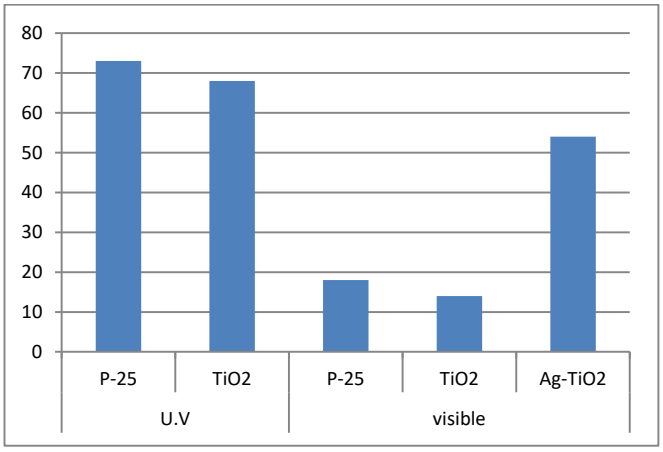

Fig. 6 COD removal efficiency

TABLE I
GC-MS RESULTS OF REACTOR INLET

Compound	RT (min)	Area (%)
dl-Limonene	5.634	2.48
13-Tertadecen-1-ol acetate	15.621	1.96
Tetramethoxyphenol	19.88	2.26
Isobutyl phthalate	20.653	6.27
Dibutyl phthalate	22.231	39.37
Beta.-H-Pregna	23.948	5
Cyclotriacontane	29.741	1.75
Beta.-H-Pregna	30.013	3.71
Bis(2-ethylhexyl) phthalate	30.685	9.2
Squalene	34.582	18.91
9-Octadecenoic acid	35.508	4.06
Triacontanol	36.851	2.14

TABLE II
GC-MS RESULTS OF REACTOR OUTLET

Compound	RT (min)	Area (%)
dl-Limonene	5.64	5.65
Alpha Terpineol	8.264	8.99
Diethyl Phthalate	15.792	6.65
Octadecene	25.438	5.29
Oleic acid	26.616	2.84
Oleic acid	27.237	2.37
Bis(2-ethylhexyl) phthalate	30.679	10.49
Squalene	34.576	27.06
Octadecenoic acid	35.818	16.42
3-Methyl-Z-14-nonacosene	36.826	5.44

In the case of doping TiO_2 with transition metals, such as Ag, due to the fact that the spectral response of TiO_2 will be in the visible region, doping such metals would increase the light reactivity of TiO_2. In addition, non-metal doped TiO_2 elements, such as carbon, nitrogen, sulfur and others, will narrow the bandgap of TiO_2, which is a significant advancement (Eg / 3 >) [24]. During the excitation of charge carriers, the lifelong of these carriers increases due to the presence of some traps in the bandgap of titanium oxide. As a consequence, we obtain an increase in the reactivity under visible light. Generally, the TiO_2 nanoparticles dispersed with metals or non-metals, or a suitable combination of both, in conjunction with a suitable metal catalyst, are found to be very suitable for applications that are sensitive to visible light [25]-[27].

IV. CONCLUSION

It has been proven that the photocatalysts, TiO_2, and Ag-TiO_2 nanoparticles, have the ability to degrade hydrocarbon pollutants in produced water, under UV light and visible light irradiation. In this study, tested samples of photocatalysts, TiO_2, and Ag-TiO_2 nanoparticles, have been successfully prepared by modified sol-gel, characterized and tested under UV and visible light irradiation. During the synthesis, CTAB surfactant was used to separate particles from each other, prevent them from joining together and causing the particles to sinter. During the re-mating process, the scattered Ag+ ions trap the electrons that are excited by light. This results in an increase in the separation between electron and hole and continuous loss of re-mating. Generally, the TiO_2 catalysts doped with a metal, a small amount of non-metal, or a suitable combination of both can be used for applications where easier sensitivity to visible light is required.

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