

Evaluation of pollutant removals from oilfield produced water using photocatalysis

Neli Mintcheva*, Gospodinka Gicheva, Marinela Panayotova

University of Mining and Geology "St. Ivan Rilski", Sofia, Bulgaria

Received August 31, 2024; Revised September 14, 2024

Nowadays, the release of hazardous compounds from wastewater into the environment is one of the major problems of sustainable development. This study aims to investigate the photocatalytic activity of nanosized ZnO and TiO₂ towards total oily hydrocarbons (TOH), phenols and chemical oxygen demand (COD) from real oilfield wastewater. The reduction of these parameters was used to evaluate the impact of photocatalyst dosage, aeration, irradiation time and pH on the effectiveness of oilfield water treatment by photocatalysis. The maximum removal of 95.2% of TOH and phenols was achieved for 12 h in the presence of ZnO with aeration of the reaction mixture. The introduction of air bubbling through the reaction system improved the removal of TOH, phenol, and COD from 93.5%, 71.7%, and 36.2% to 96.7%, 93.6%, and 75.2%, respectively, in the presence of 0.60 g/L ZnO as a photocatalyst during a 6-hour irradiation period, which was chosen as the optimal duration for photocatalysis in terms of energy and time efficiency. Under the same conditions, the elimination of TOH, phenol, and COD over TiO₂ increased from 88.1%, 6.1%, and 38.5% to 95.9%, 31.8%, and 71.9%, respectively, indicating the higher photocatalytic activity of ZnO. The pH-dependence of phenol removal over the TiO₂ photocatalyst was more pronounced than that of TOH and COD.

Keywords: oilfield wastewater; treatment; photocatalysis; ZnO, TiO₂

INTRODUCTION

The extraction of crude oil and gas from oilfield wells is accompanied by production of huge amounts of wastewater, known as produced water, which is the main waste stream in the oil industry causing significant environmental issues [1]. The produced water is a complex mixture of various organic and inorganic compounds that comprises of dissolved and dispersed hydrocarbons, benzene, toluene, ethylbenzene, xylene (BTEX), phenols, polycyclic aromatic hydrocarbons (PAHs), carboxylic acids, dissolved minerals and heavy metals, etc. [2]. Generally, physical methods are applied for separation of oil and produced water, that further is object of additional treatment to meet the requirements for the discharge in natural water bodies or for reinjection into former wells [3, 4]. The technology for produced water treatment can be divided into three categories: primary, secondary and tertiary treatment [5, 6]. In primary treatment, hydrocyclones and oil-water separators are employed to remove oil droplets and separate suspended solids, with coagulation and flocculation used to further enhance the process [7, 8]. In secondary treatment, to reduce the concentration of dispersed particles and soluble organic compounds air bubbles pass through the water container in a flotation process. Heavy metals and other dissolved compounds can be removed by adsorption as an easy-to-do method [9–12]. In biological treatment, activation sludge process is applied where bacteria

and other microorganisms are mixed with water and aerated. The tertiary treatment aims to decrease the amount of ultra-small droplets and dissolved organic and inorganic compounds by membrane technology, reverse osmosis, freeze-thaw and advanced oxidation methods [13–15]. Depending on the contaminants in the produced water, stand-alone or combination of two or more methods are applied in the treatment process [16, 17].

The increased demand for energy from fossil fuels, especially oil and gas, as well as the maturity of exploited oilfield wells lead to increasing the amount of produced water worldwide that bring about challenges for research and development of efficient purification methods for treatment of produced water not only to comply with the standards for its release into the environment but also to use the water for beneficial purposes (irrigation of crops, watering, drinking). To achieve a zero harmful regime for the environment, several treatments are available and applied, among them photocatalytic pollutant degradation is one of the innovative advanced oxidation processes [18, 19].

In photocatalysis, photochemical reactions of decomposition of organic pollutants to carboxylic/mineral acids or mineralization to CO₂ and H₂O take place in the presence of catalyst. In most cases, heterogeneous semiconductor photocatalysts such as ZnO, TiO₂, WO₃, SnO₂, etc. are irradiated with ultraviolet or visible light to generate electron-hole pairs on the surface that produce free radical oxidizing species reacting with the organic molecules. Many authors have reported

* To whom all correspondence should be sent:
E-mail: nmintcheva@mgu.bg

that photocatalysis is a promising, environmentally friendly method for the removal of oily hydrocarbons, phenols, BTEX (benzene, toluene, ethylbenzene and xylene) from oilfield wastewater [14, 20–29].

The proposed mechanism for photocatalysis over the semiconductor metal oxides consists of several steps: irradiation of oxide with energy equal to or higher than the band gap, that excites an electron to the conduction band and generates electron-hole pair; the oxygen molecules, adsorbed on the catalyst surface gain electrons and produce superoxide anion radicals ($O_2^{\cdot-}$) that oxidize the organic pollutants to less harmful molecules or mineralize them to CO_2 and H_2O . On the other side, the generated holes from the valence band of the semiconductor are available to interact with water molecules and to produce hydroxyl radicals (OH^{\cdot}) which are also able to oxidize various contaminants. The photocatalytic activity of a semiconductor strongly depends on its morphology, surface area, particle size, affecting the band gap width, which is the reason for the variety of materials with such properties. Besides, the medium, including solvent, oxygen, nature and concentration of oxidizable species, are also important for effective photocatalytic process [30, 31].

In this study, we apply photocatalysis for treatment of real oilfield produced water and investigate different factors (irradiation time, dose and type of photocatalyst, aeration, pH) affecting the photocatalytic activity of ZnO and TiO_2 for decrease of oily hydrocarbons, phenols and chemical oxygen demand.

EXPERIMENTAL

Sampling and characterization of produced water

Samples of produced water were collected from continues wastewater stream at different spots in a petroleum company located in Bulgaria. Some parameters were tested on site, while for analysis of other parameters and photocatalytic study, samples were transferred to the laboratory and stored in a

refrigerator until use. Produced water used for photocatalytic examination was analyzed for total oily hydrocarbons (TOH), phenols, chemical oxygen demand (COD) and pH before each test to obtain their initial levels. In our previous study [29], we found by GS-MS that the produced water contains saturated straight and branched hydrocarbons (C12-C22) which are well soluble in non-polar organic solvents. To characterize the organic pollutants in the produced water, we used the parameter total oily hydrocarbons (TOH) and determined the concentration of such compounds by extraction of produced water with CCl_4 . In the analytical procedure, hydrocarbons were extracted with $5\text{ cm}^3\text{ CCl}_4$ from 500 cm^3 wastewater and the absorption at 265 nm of the organic phase was measured on a BOECO UV-vis spectrophotometer [29]. The calibration curve in the range 0.02-0.10 g/dm^3 was made by using a crude oil from the same oilfield site. The phenols concentration and COD were determined spectrophotometrically by using commercial Merck tests. In the presence of an oxidizing agent, phenols and 4-aminoantipyrine form a colored product whose absorption was measured by using Spectroquant NOVA 60. The COD cell test is based on oxidation of organics by acidified $K_2Cr_2O_7$ solution and measuring the absorption of Cr(III) ions produced. More details were described previously in [29].

Immediately after sampling, physicochemical parameters were measured by using a WTW Multi 340i/SET device. Samples for dissolved oxygen were fixed on the sampling site, and O_2 concentration was determined in the laboratory by Winkler’s method. Physicochemical characteristics of produced water are summarized in Table 1. Macro- and meso-components were determined by ICP-AES, titrimetric and spectrophotometric methods [29]. Experimental values from analysis of several samples picked up from various points of the petroleum plant are listed in Table 2. Only some of the collected samples were used for photocatalytic treatment presented in this paper.

Table 1. Physicochemical parameters (temperature, pH, redox potential, conductivity and dissolved oxygen) of the produced water.

Parameter	T, °C	pH	Eh, mV	χ , mS/cm	Dissolved O_2 , mg/L
Range	10-26	7.6-9.2	78-386	1.3-7.0	0.1-5.7

Table 2. Range of concentrations (in mg/L) of macro- and meso-components and specific parameters of the produced water.

Parameter	Ca^{2+}	Mg^{2+}	Na^+	Cl ⁻	HCO_3^-	SO_4^-	H_2S	TOH	Phenol	COD
Range	56-176	8-58	370-1644	640-2812	59-189	45-123	0.6-22.0	4-540	1.0-5.0	60-1800

Photocatalytic tests

Photocatalysts used. The photocatalysts ZnO and TiO₂ used in this study were purchased from Reachim, Chimspectar, Sofia and Riedel-de-Haen, Seelze. Anatase phase of TiO₂ and wurtzite ZnO with average particle size of 33 nm and 30 nm for TiO₂ and ZnO, respectively, were determined by XRD analysis. The band gap of 3.48 eV and 3.25 eV for TiO₂ and ZnO, respectively, was estimated from Tauc's plot of their diffuse reflectance UV-vis spectra [29].

In a general procedure, a certain amount of photocatalyst (listed below) was loaded into 500 mL produced water, the mixture was kept in dark for 30 minutes under constant stirring and then irradiated with UV light.

Dose range (0.08 – 2.40 g/L). To determine the optimal dose of ZnO and TiO₂ for treatment of the produced water, the removal of TOH, phenol and COD was examined in the experiments, using the following amount of the photocatalyst: 0.08; 0.15; 0.30; 0.60; 1.20; 2.40 g/L, while keeping constant the UV irradiation for 6 hours (by UV lamp 18 W, 365 nm) and total volume of treated sample.

Aeration of the reaction mixture. To evaluate the effect of aeration on the elimination of organic pollutants, two series of tests were carried out – one without air bubbling, and the second one with constant air flow at a rate of 120 L/h. The photocatalyst in the range (0.08 – 2.40 g/L) was used and the irradiation time was 6 hours.

Duration of irradiation. To determine the optimum treatment time, the removal of TOH and phenol was studied by using a dose of 0.30 g/L ZnO (or TiO₂), air supply from aeration pump and UV irradiation for 0 – 14 hours. The analysis of TOH and phenol was performed at 3rd, 6th, 8th, 12th and 14th hour.

pH change. During the experiments for studying the effect of pH, the acidity of the produced water was adjusted at pH values 3, 5, 7, 10 by using HCl or NaOH solutions. The dose of photocatalyst was

0.30 g/L ZnO (or TiO₂), the irradiation lasted for 6 h and air was not supplied.

In all cases, the removal of TOH, phenol and COD was calculated by the formula:

$$removal = \frac{C_o - C_i}{C_o} \cdot 100, \%$$

where C_i is the concentration at a certain time and C_o is the initial concentration.

RESULTS AND DISCUSSION

Effect of photocatalyst dosage and aeration

As mentioned above, the adsorption of oxygen molecules on the photocatalyst's surface is crucial for the effective process. However, analysis of the studied produced water showed that it contains low concentration of dissolved oxygen (Table 1), that's why we applied two ways to enrich the reaction mixture with oxygen – by agitating in air and by bubbling air through the reaction mixture. Two sets of samples containing semiconductor metal oxide (ZnO or TiO₂) in doses from 0.08 to 2.40 g/L were performed. The data for TOH, phenol and COD removal in the presence of ZnO and TiO₂ without aeration of the reaction mixture are presented in Table 3 and Table 4, respectively. The results from the second series obtained by aeration are shown in Table 5 and Table 6 for ZnO and TiO₂, respectively.

The photocatalytic treatment was carried out in an open-air system under continuous stirring that allows oxygen molecules to enter aqueous solution and to facilitate the photocatalytic process. In Figure 1, one can see that an optimum ZnO catalyst dose is around 0.6 g/L which causes removal of TOH, phenol and COD ca. 94%, 72% and 36%, respectively in the presence of oxygen from the air (without air bubbling). Increasing the amount of ZnO four times promotes the elimination of pollutants with 2%, 10% and 8% for the respective parameters. The higher activity relates to increasing the catalyst surface area with increasing its dose, but above a certain amount of photocatalyst its action becomes independent from the concentration.

Table 3. Data for TOH, phenol and COD removal in the presence of ZnO (doses 0.08-2.40 g/L) for 6 h irradiation time, without aeration of the reaction mixture. Initial pH of produced water 7.8. * in (mg/L); ■ in (%)

Dose g/L	TOH			Phenol			COD		
	in*	final*	removal ■	in*	final*	removal ■	in*	final*	removal ■
0.08	82.6	27.1	67.2	1.31	0.74	43.5	130	88	32.3
0.15	82.6	16.5	80.0	1.31	0.53	59.5	130	85	34.6
0.30	82.6	12.5	84.9	1.31	0.48	63.4	130	84	35.4
0.60	82.6	5.4	93.5	1.31	0.37	71.7	130	83	36.2
1.20	82.6	3.7	95.5	1.31	0.31	76.3	130	82	36.9
2.40	82.6	3.0	96.4	1.31	0.24	81.7	130	72	44.6

Table 4. Data for TOH, phenol and COD removal in the presence of TiO₂ (doses 0.08-2.40 g/L) for 6 h irradiation time, without aeration of the reaction mixture. Initial pH of produced water 7.8.

Dose g/L	TOH			Phenol			COD		
	in*	final*	removal ▪	in*	final*	removal ▪	in*	final*	removal ▪
0.08	82.6	13.6	83.5	1.31	1.30	0.8	130	84	35.4
0.15	82.6	13.3	83.9	1.31	1.26	3.8	130	83	36.2
0.30	82.6	11.7	85.8	1.31	1.25	4.6	130	83	36.2
0.60	82.6	9.8	88.1	1.31	1.23	6.1	130	80	38.5
1.20	82.6	6.6	92.0	1.31	1.21	7.6	130	79	39.2
2.40	82.6	3.5	95.8	1.31	1.00	23.7	130	77	40.8

* in (mg/L); ▪ in (%)

Table 5. Data for TOH, phenol and COD removal in the presence of ZnO (doses 0.08-2.40 g/L) for 6 h irradiation time, with aeration of the reaction mixture. Initial pH of produced water 7.6.

Dose g/L	TOH			Phenol			COD		
	in*	final*	removal ▪	in*	final*	removal ▪	in*	final*	removal ▪
0.08	471.9	105.1	77.7	1.10	0.57	48.2	303	128	57.8
0.15	471.9	44.8	90.5	1.10	0.31	71.8	303	98	67.7
0.30	471.9	21.6	95.4	1.10	0.11	90.0	303	79	73.9
0.60	471.9	15.6	96.7	1.10	0.07	93.6	303	75	75.2
1.20	471.9	6.4	98.6	1.10	0.05	95.4	303	72	76.2
2.40	471.9	5.1	98.6	1.10	0.01	99.1	303	69	77.2

* in (mg/L); ▪ in (%)

Table 6. Data for TOH, phenol and COD removal in the presence of TiO₂ (doses 0.08-2.40 g/L) for 6 h irradiation time, with aeration of the reaction mixture. Initial pH of produced water 7.6.

Dose g/L	TOH			Phenol			COD		
	in*	final*	removal ▪	in*	final*	removal ▪	in*	final*	removal ▪
0.08	471.9	45.1	90.4	1.10	1.05	4.5	303	115	62.0
0.15	471.9	33.4	92.9	1.10	0.95	13.6	303	95	68.6
0.30	471.9	25.2	94.6	1.10	0.79	28.2	303	88	70.9
0.60	471.9	19.1	95.9	1.10	0.75	31.8	303	85	71.9
1.20	471.9	8.7	98.1	1.10	0.70	36.3	303	83	72.6
2.40	471.9	4.2	99.1	1.10	0.65	40.9	303	82	73.0

* in (mg/L); ▪ in (%)

To evaluate the effect of additional O₂ stream into the system, we carried out experiments when air was bubbling through the reaction mixture by aeration pump.

In Fig. 1 (right side) we observed higher removal degree for all studied parameters and significant decrease of COD in the effluent. Both COD and phenols are associated with dissolved organics, indicating that their concentrations decrease upon photocatalysis, while TOH is responsible for extractable ultra-small droplets of finely dispersed non-polar hydrocarbons, that were efficiently degraded over ZnO surface under UV light irradiation [32]. The latter parameter is slightly affected by introducing additional oxygen in the system. Similar

trends were observed for TiO₂ photocatalysis (Fig. 2), confirming the advantage of air bubbling during the treatment. It is worth mentioning that the optimal catalyst dose also decreases upon aeration, and sufficient removal can be achieved with amount of 0.3 g/L for both ZnO and TiO₂ [33]. Therefore, more efficient removal of contaminants was achieved when air was bubbling through the reaction mixture (Fig. 1 and Fig. 2). This effect is more pronounced for ZnO. As can be seen on the right-side graphs of Fig. 1 and Fig. 2 the photocatalytic activity of ZnO is higher than that of TiO₂ [34].

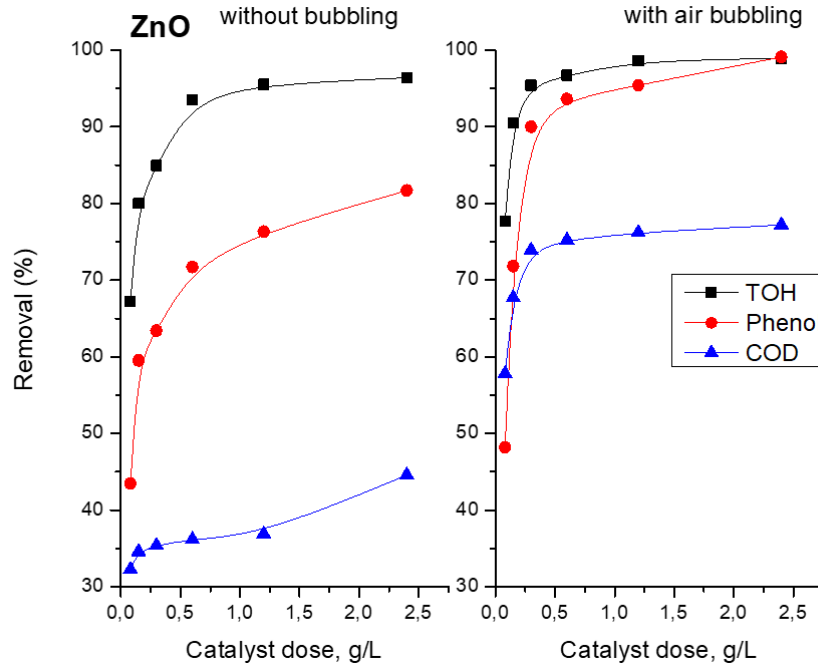


Figure 1. Dose-dependence of TOH, phenol and COD removal over ZnO photocatalyst with and without aeration of the system for 6 h irradiation time.

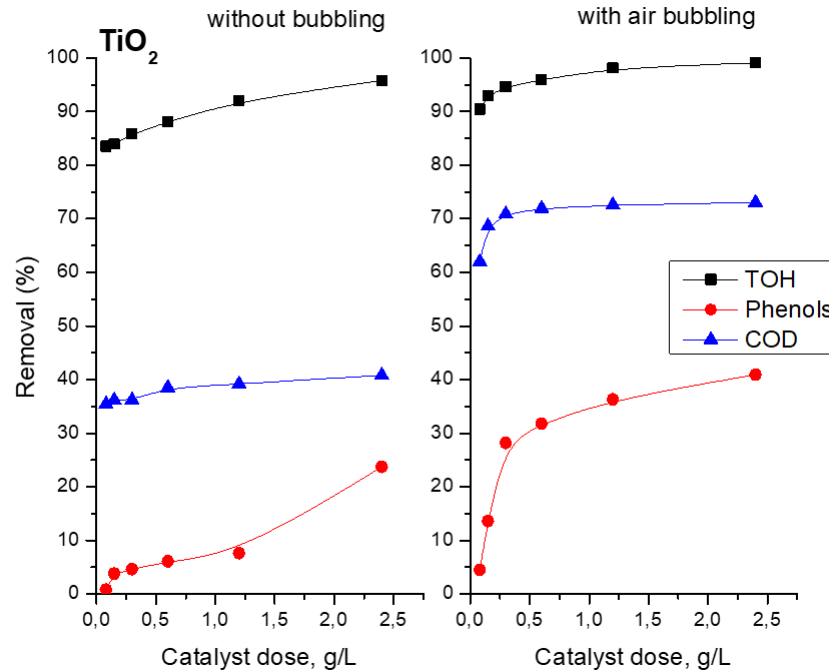


Figure 2. Dose-dependence of TOH, phenol and COD removal over TiO₂ photocatalyst with and without aeration of the system for 6 h irradiation time.

Effect of irradiation time. The evaluation of time duration for photocatalytic degradation of pollutants was performed by following the changes in TOH and phenol levels over ZnO and TiO₂ photocatalysts (dose 0.30 g/l), under air bubbling and UV irradiation. Data for ZnO and TiO₂ are presented in Table 7 and Table 8, respectively. As an optimal irradiation time was chosen 6 h when the removal was 84.0% and 90.3% for TOH and phenol, respectively over the catalyst ZnO (Fig. 3).

The removal of TOH and phenol in the presence of TiO₂ for 6 h was 80.5% and 29.1%, respectively. Obviously, TiO₂ demonstrates lower photocatalytic activity for the studied time interval (Fig. 3) [22, 23]. Maximum removal for both catalysts was observed after 12-14 hours irradiation. However, due to energy-saving and time-saving reasons, which are very important for practical applications, prolonged treatment was not recommended.

Table 7. Data for TOH and phenol removal in the presence of ZnO with aeration of the reaction mixture for a duration up to 14 hours. Initial pH of produced water 7.8.

Time. h	TOH			Phenol		
	in*	final*	removal▪	in*	final*	removal▪
3	14.71	7.93	46.1	1.65	0.80	51.5
6	14.71	2.35	84.0	1.65	0.16	90.3
8	14.71	0.97	93.4	1.65	0.09	94.5
12	14.71	0.70	95.2	1.65	0.08	95.2
14	14.71	0.34	97.7	1.65	0.08	95.2

* in (mg/L); ▪ in (%)

Table 8. Data for TOH and phenol removal in the presence of TiO₂ with aeration of the reaction mixture for a duration up to 14 hours. Initial pH of produced water 7.6

Time. h	TOH			Phenol		
	in*	final*	removal▪	in*	final*	removal▪
3	26.3	9.94	62.2	1.65	1.40	15.1
6	26.3	5.12	80.5	1.65	1.17	29.1
8	26.3	3.69	86.0	1.65	1.14	30.9
12	26.3	2.77	89.5	1.65	1.01	38.8
14	26.3	1.62	93.8	1.65	0.96	41.8

* in (mg/L); ▪ in (%)

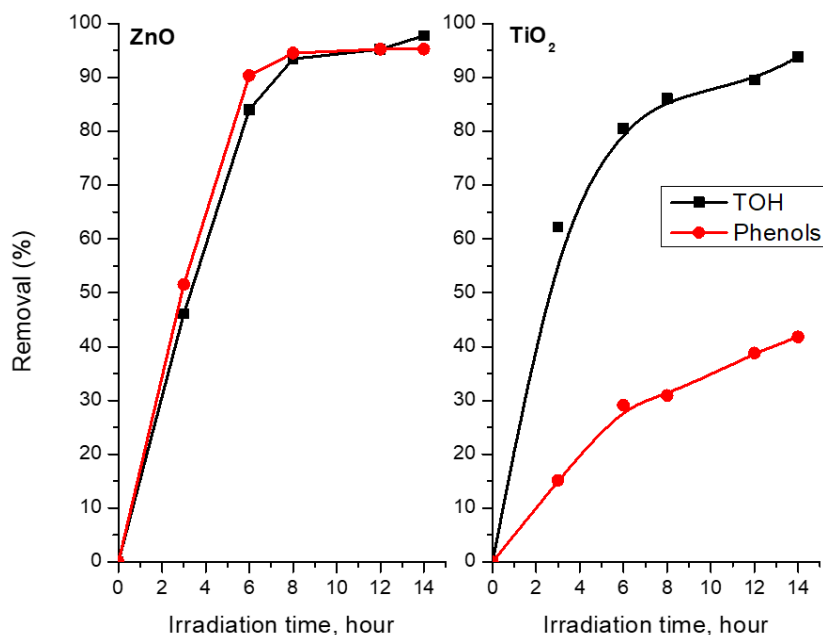


Figure 3. Time-dependence of TOH and phenol removal over ZnO and TiO₂ photocatalyst (0.30 g/L) with aeration of the system.

Effect of pH. Influence of initial pH on the TOH, phenols and COD concentrations was investigated. The catalyst load was 0.30 g/L, irradiation time was 6 h, and air was not bubbling through the reaction mixture. Collected data is listed in Tables 9 and 10 for ZnO and TiO₂ catalyst, respectively. Fig. 4 shows the trend of all parameters indicating minimal removal percent at neutral pH and maximum removal around pH 4 for ZnO and around pH 5 for TiO₂. Despite the similar activity of both photocatalysts towards TOH and COD, the phenol removal profile deserves further discussion. In the case of ZnO, the phenols removal

increases around 20% in acidic medium compared to neutral solution, while for TiO₂ photocatalyst decomposition enhanced by 37%. We assume that in both materials such difference is due to changes on the surface of the solid catalyst and adsorption ability of contaminant species.

In photocatalysis, the pH of aqueous solution affects the surface charge of nanoparticles (isoelectric point), its solubility, size and band gap due to interactions of H⁺/OH⁻ with metal oxides [35]. Many reports study the point of zero charge of semiconductors as a function of pH to explain their photocatalytic performance [21]. The pH equal to

the zero-surface charge of TiO₂ was determined in the range of 4.5 to 7.0, depending on the catalyst characteristics [30]. At this point the electrostatic forces between solid catalyst and contaminants are weak. When pH is lower, H⁺ ions are adsorbed on the surface and formed its positive charge, thus attracting negatively charged particles. Phenols are dissociated in aqueous solution and phenolate anions are adsorbed onto UV-activated TiO₂ surface where radical-oxidative reactions undergo resulting in increased photodegradation. When pH of solution is alkaline the effect on photocatalysis is more complicated, as on one side the TiO₂ surface is negatively charged repelling anionic species and attracting positively charged contaminants, but from other side OH⁻ ions form active hydroxyl

radicals which are engaged in oxidation of organics.

As can be seen in Table 10, the pH levels at the end of the treatment are very close to the initial one, showing stability of acidity during the photocatalytic process. In contrast, pH tends to reach neutral values (except for pH 10) for ZnO (Table 9), which can be explained by the amphoteric properties of ZnO that reacts with H⁺ ions [36]. Obviously, such changes modify the surface charge of ZnO nanoparticles and reduce the effect of initial pH on the pollutant's removal.

Although pH-dependence was observed, the initial pH was not adjusted for other photocatalytic experiments in this study. It could be taken into account in future investigations, in order to maximize the effectiveness of the photocatalysis.

Table 9. Data for TOH, phenol and COD removal in the presence of ZnO at different initial pH values. Catalyst dose is 0.30 g/L, irradiation time 6 h, without aeration of the system.

pH in	pH out	TOH			Phenol			COD		
		in*	final*	removal▪	in*	final*	removal▪	in*	final*	removal▪
3	6.8	44.7	2.35	94.7	1.57	0.48	69.4	160	87	45.6
5	6.7	44.7	1.86	95.8	1.57	0.51	67.5	160	86	46.2
7	7.2	44.7	7.64	82.9	1.57	0.76	51.6	160	97	39.4
10	9.1	44.7	1.97	95.6	1.57	0.71	54.8	160	82	48.8

* in (mg/L); ▪ in (%)

Table 10. Data for TOH, phenol and COD removal in the presence of TiO₂ at different initial pH values. Catalyst dose is 0.30 g/L, irradiation time 6 h, without aeration of the system.

pH in	pH out	TOH			Phenol			COD		
		in*	final*	removal▪	in*	final*	removal▪	in*	final*	removal▪
3	3.14	44.7	3.75	91.6	1.57	0.84	46.5	160	86	46.2
5	5.40	44.7	3.08	93.1	1.57	1.05	33.1	160	81	49.4
7	7.34	44.7	7.01	84.3	1.57	1.42	9.6	160	92	42.5
10	9.67	44.7	5.42	87.2	1.57	1.22	22.3	160	81	49.4

* in (mg/L); ▪ in (%)

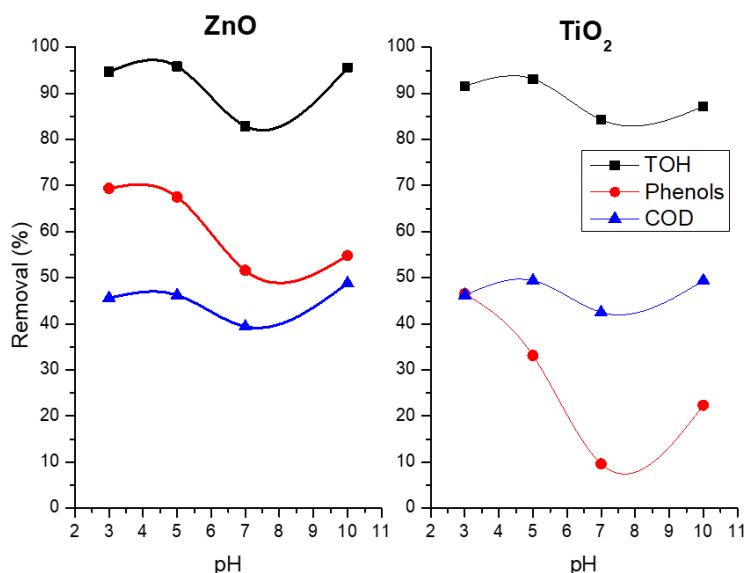


Figure 4. pH-dependence of TOH, phenol and COD removal over ZnO and TiO₂ photocatalyst (0.30 g/L) for 6 h irradiation and without aeration of the system.

CONCLUSIONS

The photocatalysts ZnO and TiO₂ were proven as a good choice for UV-induced removal of TOH, phenols and COD from real oilfield produced water. The performance of ZnO is superior to that of TiO₂, especially for phenols reduction. The photocatalytic process was significantly improved by aeration of the reaction mixture at neutral values of pH. The highest effect of pH was observed on the phenol removal over TiO₂, which varies from 9.6% at pH 7 to 46.5% at pH 3 for 6 hours irradiation and without additional supply of oxygen. The optimum conditions for the photocatalytic process found in this study are a dosage of ZnO (TiO₂) of 0.30 g/L, air flow with rate of 120 L/h, irradiation time 6 hour and neutral to slightly acidic pH. This research provides an effective method for tertiary treatment of oilfield produced water from industrial sites for sustainable utilization of their wastewater streams.

Acknowledgement. This research was financially supported by the University of Mining and Geology, grand number MTF-197/2024.

REFERENCES

- B. Sanchez, „Fossil fuels account for the largest share of U.S. energy production and consumption “*Today in Energy*, U.S. Energy Information Administration, (2020). <https://www.eia.gov/todayinenergy/detail.php?id=45096>. (accessed on 11 August 2024).
- A. Fakhru'l-Razi, A. Pendashteh, L.C. Abdullah, D.R.A. Biak, S.S. Madaeni, Z.Z. Abidin, *J. Hazard. Mater.* **170**, 530 (2009). <https://doi.org/10.1016/j.jhazmat.2009.05.044>.
- E. T. Igunnu, G.Z. Chen, *Int. J. Low-Carbon Technol.* **9**, 157 (2014). [<https://doi.org/10.1093/ijlct/cts049>].
- M. Nasiri, I. Jafari, *Period. Polytech. Chem. Eng.* **61**, 73 (2017). <https://doi.org/10.3311/PPch.8786>.
- K. T. Amakiri, A. R. Canon, M. Molinari, *Chemosphere*, **298**, 134064 (2022). <https://doi.org/10.1016/j.chemosphere.2022.134064>.
- A.A. Olajire, *Chem. Eng. J. Adv.*, **4**, 100049 (2020). <https://doi.org/10.1016/j.ceja.2020.100049>.
- O. Okoro, I. Papineau, M. Sollicec, L. Fradette, B. Barbeau, *Sci. Total Environ.* **801**, 149583 (2021), <https://doi.org/10.1016/j.scitotenv.2021.149583>.
- G. Hu, J. Li, G. Zeng, *J. Hazard. Mater.* **261**, 470 (2013). <https://doi.org/10.1016/j.jhazmat.2013.07.069>.
- D. Gkogkou, S. Rizogianni, Ch. Tziasiou, V. Gouma, A. D. Pournara, D. Tsoukleris, D. L. Giokas, M. J. Manos, *J. Environ. Chem. Eng.* **9**, 106170; 1 (2021). <https://doi.org/10.1016/j.jece.2021.106170>.
- R. Wahi, L. A. Chuah, T.S.Y. Choong, Z. Ngaini, M.M. Nourouzi, *Sep. Purif. Technol.*, **113**, 51 (2013). <http://dx.doi.org/10.1016/j.seppur.2013.04.015>.
- J. O. Nwadiogbu, V. I. E. Ajiwe, P. A. C. Okoye, *J. Taibah Univ. SCI*, **10**, 56 (2016) <http://dx.doi.org/10.1016/j.jtusc.2015.03.014>.
- S. Gupta, N.-H. Tai, *J. Mater. Chem. A*, **4**, 1550 (2016). <https://doi.org/10.1039/C5TA08321D>.
- Y. Xu, D. Yuan, Y. Guo, Sh. Chen, W. Lin, Y. Long, J. Bao, C. He, C. Cheng, C. Deng, Y. Zhang, Y. Wu, W. Zhao, C. Zhao, *Chem. Eng. J.*, **427**, 131685 (2022). <https://doi.org/10.1016/j.cej.2021.131685>.
- D. Cazzoir, L. Fine, C. Ferronato, J.-M. Chovelon, *J. Hazard. Mater.*, **235–236**, 159 (2012). <http://dx.doi.org/10.1016/j.jhazmat.2012.07.037>.
- F.V. Santos, E.B. Azevedo, G.L. Sant'Anna Jr., M. Dezotti, *Braz. J. Chem. Eng.*, **23**, 451 (2006). <https://doi.org/10.1590/S0104-66322006000400003>.
- X. Dai, J. Fang, L. Li, Y. Dong, J. Zhang, *Int. J. Environ. Res. Public Health*, **16**, 3223 (2019). <https://doi.org/10.3390/ijerph16173223>.

17. G. Li, S. Guo, F. Li, *J. Environ. Sci.*, **22**, 1875 (2010). [https://doi.org/10.1016/S1001-0742\(09\)60333-8](https://doi.org/10.1016/S1001-0742(09)60333-8).
18. H. Zhang, Ch. Gao, H. Zhang, N. Song, Q. Cao, *Water Reuse*, **14(2)**, 190 (2024). <https://doi.org/10.2166/wrd.2024.003>.
19. L. Lin, W. Jiang, L. Chen, P. Xu, H. Wang, *Catalysts*, **10**, 924 (2020). <https://doi.org/10.3390/catal10080924>.
20. S. M. King, P. A. Leaf, A.C. Olson, P. Z. Ray, M.A. Tarr, *Chemosphere*, **95**, 415 (2014). <https://doi.org/10.1016/j.chemosphere.2013.09.060>.
21. J. Saien, F. Shahrezaei, *Int. J. Photoenergy*, **2012**, 703074 (2012). <https://doi.org/10.1155/2012/703074>.
22. E.B. Azevedo, A.R. Tôrres, F.R. Aquino Neto, M. Dezotti, *Braz. J. Chem. Eng.*, **26**, 75 (2009). <https://doi.org/10.1590/S0104-66322009000100008>
23. E.K. Tetteh, S. Rathilal, D.B. Naidoo, *Sci. Rep.*, **10**, 8850 (2020). <https://doi.org/10.1038/s41598-020-65480-5>
24. G.R. Soltanian, M. Havaee Behbahani, *Iran. J. Environ. Health Sci. Eng.*, **8**, 169 (2011).
25. W.Z. Khan, I. Najeeb, M. Tuiyebayeva, Z. Makhtayeva, *Process Saf. Environ. Prot.*, **94**, 479 (2015). <https://doi.org/10.1016/j.psep.2014.10.007>.
26. A.A. Hassan, H.T. Naeema, R.T. Hadi, *Pak. J. Biotechnol.*, **15**, 909 (2018).
27. J. Al-Sabahi, T. Bora, M. Al-Abri, J. Duta, *PLoS ONE*, **12**, e0189276 (2017). <https://doi.org/10.1371/journal.pone.0189276>.
28. P. Azmoon, M. Farhadian, A. Pendashteh, S. Tangestaninejad, *Appl. Surf. Sci.*, **613**, 155972, (2023). <https://doi.org/10.1016/j.apsusc.2022.155972>.
29. N. Mintcheva, G. Gicheva, M. Panayotova, *Pollutants*, **2**, 234 (2022). <https://doi.org/10.3390/pollutants2020016>.
30. M. N. Chong, B. Jin, C. W. Chow, C. Saint, *Water Res.*, **44**, 2997 (2010). <https://doi.org/10.1016/j.watres.2010.02.039>.
31. K.M. Lee, C.W. Lai, K.S. Ngai, J.C. Juan, *Water Res.*, **88**, 428 (2016). <https://doi.org/10.1016/j.watres.2015.09.045>.
32. J. Lu, X. Wang, B. Shan, X. Li, W. Wang, *Chemosphere*, **62**, 322 (2006). <https://doi.org/10.1016/j.chemosphere.2005.04.033>.
33. D. A. Aljuboury, P. Palaniandy, H.B. Abdul Aziz, S. Feroz, S.S. Abu Amr. *Water Sci Technol.* **74(6)**,1312 (2016). doi: 10.2166/wst.2016.293.
34. H.A.J. Alkhazraji, M.J.A. Alatabe, *J. Ecol. Eng.*, **22**, 278 (2021). <https://doi.org/10.12911/22998993/140281>.
35. J. Miao, Z. Jia, H.-B. Lu, D. Habibi, L.-C. Zhang, *J. Taiwan Inst. Chem. E.*, **45(4)**, 1636 (2014), <https://doi.org/10.1016/j.jtice.2013.11.007>.
36. C. F. Klingshirn, A. Waag, A. Hoffmann, J. Geurts. *Zinc Oxide: From Fundamental Properties Towards Novel Applications*. Springer Science & Business Media, Technology & Engineering. 2010.