Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2016, Article ID 8471960, 7 pages
http://dx.doi.org/10.1155/2016/8471960

Research Article

Laboratory and Pilot-Plant Scale Photocatalytic Degradation of Polychlorinated Biphenyls in Seawater Using CM-n-TiO_2 Nanoparticles

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Received 23 January 2016; Accepted 11 April 2016

Academic Editor: Lei Zhang

Photocatalytic degradation of polychlorinated biphenyls (PCBs) in seawater was successfully achieved at laboratory level with UV light and at pilot-plant scale under natural solar radiation using carbon-modified titanium oxide (CM-n-TiO_2) nanoparticles. The photocatalytic performance of CM-n-TiO_2 was comparatively evaluated with reference n-TiO_2 under identical conditions. As a result of carbon incorporation, significant enhancement of photodegradation efficiency using CM-n-TiO_2 was clearly observed. To optimize the operating parameters, the effects of catalyst loading and pH of the solution on the photodegradation rate of PCBs were investigated. The best degradation rate was obtained at pH 5 and CM-n-TiO_2 loading of 0.5 g L^{-1}. The photodegradation results fitted the Langmuir-Hinshelwood model and obeyed pseudo-first-order reaction kinetics.

1. Introduction

Polychlorinated biphenyls (PCBs) are a class of persistent organic pollutants that are ubiquitous in the environment. USEPA has classified PCBs as compounds with significant human health risk, due to their toxicity, carcinogenicity, and bioaccumulation nature [1]. Therefore, the release of these pollutants into water resources poses a serious threat to human health and the environment [2]. Though their production has been prohibited, they are still remaining in large quantities in industrial fluids, heat exchangers, and plasticizers.

Incineration is the main remediation technology for PCBs. However, it demands expensive facilities and high temperatures of more than 1200°C [3]. Recently, heterogeneous photocatalytic technology involving TiO_2 semiconductor under light irradiation has shown potential advantages to be used as an alternative remedial technology, because it is inexpensive and can rapidly and completely mineralize organic pollutants. TiO_2 has been studied extensively for practical utilization for water splitting [4, 5], remedy of many organic pollutants [6–9], and treatment of wastewater [10–12]. However, TiO_2 photocatalysis is limited to UV light, as a result of its wide bandgap (3.0–3.2 eV). To overcome this drawback, several studies have been performed to modify TiO_2 with nitrogen [13, 14], sulfur [15], and transition metal [16, 17] to extend its photoresponse to the visible region by narrowing its bandgap energy. Recently, it has been evidently demonstrated that modification of TiO_2 by carbon enhanced its photoresponse by narrowing its bandgap energy [4–6]. In our previous work [9], we have successfully synthesized carbon-modified TiO_2 photocatalyst with low bandgap energy of 1.8 eV. Compared to unmodified TiO_2, the synthesized photocatalyst showed significantly higher activity towards the photocatalytic degradation of PCBs in aqueous solution under illumination of UV light.

Although photocatalytic remediation of contaminated water has been extensively studied using UV/n-TiO_2 at laboratory scale, relatively few attempts have been carried out at pilot-plant scale under natural sunlight. To the best of our knowledge, no study has been focused specifically on the photocatalytic removal of PCBs from seawater using CM-n-TiO_2 at solar-driven pilot-plant scale. Therefore, it could be of interest for environmental and economic considerations to evaluate the possibility of exploitation of the renewable solar energy through the utilization of pilot plant for the purification of polluted water.

In this context, this work aimed at studying the degradation efficiency of polychlorinated biphenyls (PCBs) in seawater using CM-n-TiO_2 nanoparticles at laboratory scale under artificial UV light as well as evaluating the viability and the performance of the pilot plant for the remediation of these compounds under natural sunlight. The experimental conditions including CM-n-TiO_2 loading and solution pH were optimized at the lab scale and were applied for the solar pilot plant.

2. Materials and Methods

2.1. Catalyst Preparation and Characterization. CM-n-TiO_2 nanoparticles were fabricated by sonicated sol-gel method using titanium(IV) isopropoxide as a titanium and carbon-containing precursor. The preparation and characterization of CM-n-TiO_2 have been reported in detail elsewhere [9]. Reference n-TiO_2 (Loba Chemie Pvt. Ltd., extra pure, India) was used for comparison.

2.2. Photocatalytic Removal Experiments. Clean seawater samples, collected from Sharm Obhur, Jeddah Red Sea coast, were spiked with various concentrations of PCBs (Aroclor 1254 and Aroclor 1260). Photocatalytic degradation experiments were performed at laboratory level with UV light and at pilot-plant scale with natural solar radiation. The effects of operating parameters including CM-n-TiO_2 loading and pH of the solution on the photodegradation rate of PCBs have been investigated first at lab scale to reach the optimum conditions and then were applied at pilot-plant scale.

2.2.1. Lab Scale. For lab scale photocatalytic experiments, a 500 mL Pyrex glass reactor was used as a batch reactor under illumination of UV light. Both contaminated samples and the photocatalyst were loaded inside the photocatalytic reactor and continuously stirred for uniform mixing. Prior to light irradiation, the suspensions were equilibrated for 30 min in the dark. Then, the photoreactor was irradiated with low pressure UV fluorescent lamp (Upland, 15 W of wavelength 365 nm) placed inside Fluorescence Cabinet (CC-80, Spectroline).

2.2.2. Pilot-Plant Scale. Solar pilot-plant scale reactor, so-called Solar Falling Film Reactor (SFFR), was designed and built. The performance of the CM-n-TiO_2/SFFR system was evaluated towards the photocatalytic removal of PCBs under real sunlight illumination. The SFFR consists of flat tray, top distributor, bottom collector, a pump (Pedrollo, Italy, model: PKm 60-BR, 550 W), and a batch tank (equipped with electric mixer to allow homogenization) located underneath the flat tray (Figure 1). The flat tray, top distributor, and bottom collector are made of stainless steel, Grade 316, to avoid rust problems that may affect the measurements. The flat tray is about 1.0 m wide by 1.5 m length with 10 cm side height. The fluid flows from the tank using the pump to the top distributor of the SFFR down to the flat tray to the bottom collector and back to the tank again; the water thus continuously circulates in a closed circuit. The flow rate is adjusted by a by-pass valve. The flat tray is mounted on a stainless steel stand with pivot allowing accurate adjustment of the tilt angle; the tilt angle was adjusted to be $22^\circ \pm 10^\circ$ for maximum solar collection in Jeddah. The SFFR has an irradiated surface of 1.5 m^2 and total volume of 20 L. The experiments were carried out on sunny days between 11:00 a.m. and 3:00 p.m. The average solar intensity was 1140 Wm^{-2}, measured by Field Scout Light Sensor Reader (Spectrum Technologies, Inc.) equipped with 3670i Silicon Pyranometer Sensor.

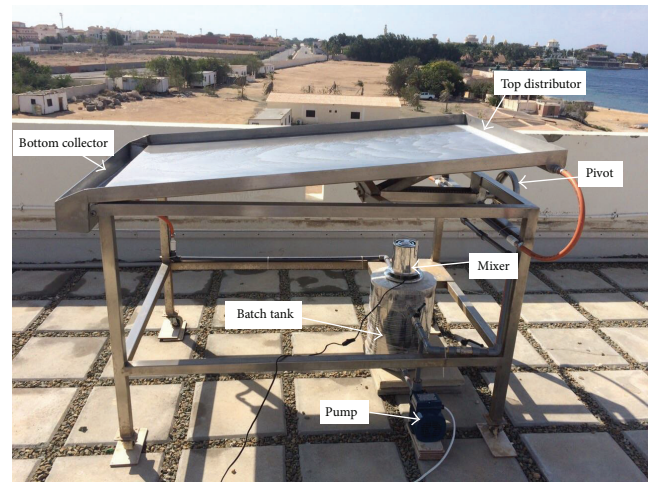

Figure 1: Photograph of the Solar Falling Film Reactor (SFFR).

2.3. Analysis. Treated PCBs solution was sampled at regular irradiation intervals. The samples containing photocatalyst were centrifuged for 5 minutes and then the supernatant was shaken with 2 mL of a mixture of hexane and dichloromethane (1 : 1) for 15 min. Using a nitrogen evaporator, extracted samples were concentrated to 0.5 mL and then transferred to screw capped vials and stored at 4°C before analysis. The concentration of PCBs (Ar 1254 and Ar 1260) was measured using gas chromatograph coupled with ^{63}Ni electron capture detector (GC-ECD, Shimadzu 2010). Rxi-XLB capillary column (30 m × 0.32 mm × 0.5 μm) was used. The injection port temperature was held at 250°C and the detector temperature was kept at 320°C. A constant flow rate of 1.7 mL/min was applied for carrier gas. The volume of 2.0 μL was used for injection. The temperature of the oven was held at 100°C for 1 min, ramped up to 270°C at rate of 30°C/min, and maintained for 1 min and finally ramped up to 300°C at rate of 2.0°C/min and kept for 3 min. The PCBs

Table 1: Optical properties of CM-n-TiO_2 and n-TiO_2 nanoparticles.

Catalyst	Crystal phase	Crystalline size (nm)	Bandgap (eV)	Atomic %		
				Ti	O	C
CM-n-TiO_2	Anatase	31.4	1.8	29.81	61.21	8.98
n-TiO_2	Anatase	41.5	2.99	36.54	63.46	00.00

were identified by comparison of retention time using series of PCBs standards. The removal efficiency (R%) is calculated as follows:

$$R\% = \frac{A_0 - A_t}{A_0} \times 100, \quad (1)$$

where A_0 and A_t are the peak areas of PCBs before (i.e., at zero time) and after irradiation at (t) time, respectively.

3. Results and Discussion

3.1. Photocatalyst Characterization. In our previous work [9], carbon-modified titanium oxide (CM-n-TiO_2) and unmodified titanium dioxide (n-TiO_2) nanoparticles were characterized in detail. Table 1 summarizes the optical properties of each catalyst. As can be seen, the incorporation of carbon (8.98 atomic %) into CM-n-TiO_2 lowered the bandgap energy from 2.99 to 1.8 eV. Therefore, it is expected that CM-n-TiO_2 will have higher photocatalytic activity than n-TiO_2 in both UV and visible regions.

3.2. Photocatalytic Degradation at Laboratory Scale

3.2.1. Effect of Catalyst Loading. The effect of CM-n-TiO_2 dose on the photocatalytic degradation of a mixture of Ar 1254 (0.5 ppm) and Ar 1260 (0.5 ppm) in seawater under illumination of UV light was studied to attain the optimum catalyst loading (Figure 2). It is clearly noted that the increase in the amount of catalyst from 0.25 g L^{-1} to 0.5 g L^{-1} increases the photocatalytic degradation rate due to the increase of the number of hydroxyl radicals. Further increase in the catalyst loading leads to the reduction of the degradation rate, revealing optimum catalyst loading of 0.5 g/L. The observed decrease in degradation rate can be attributed to the agglomeration of catalyst particles in addition to the light shading by the suspension [18, 19].

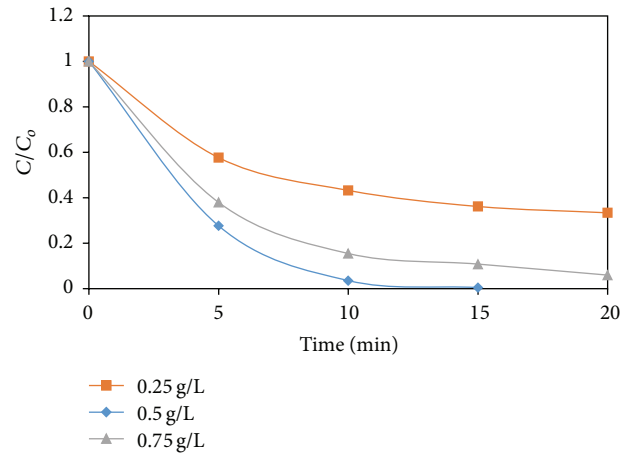

Figure 2: Effect of catalyst dose on the photocatalytic degradation of mixture of Ar 1254 (0.5 ppm) and Ar 1260 (0.5 ppm) in seawater under illumination of UV light.

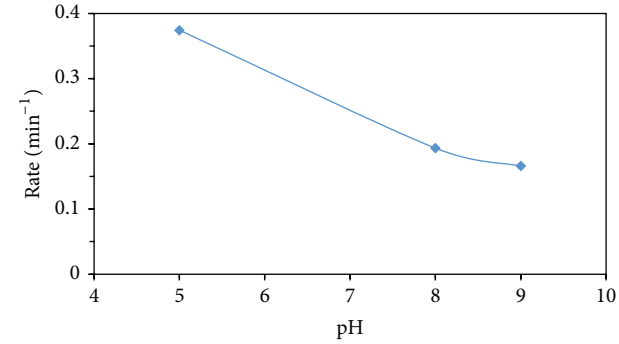

Figure 3: Effect of pH on the photocatalytic degradation of mixture of Ar 1254 (0.5 ppm) and Ar 1260 (0.5 ppm) in seawater using 0.5 g L^{-1} of CM-n-TiO_2 under illumination of UV light.

3.2.2. Effect of pH. The effect of pH on the photodegradation of PCBs in seawater under illumination of UV using CM-n-TiO_2 was studied at three different pH values 5, 7, and 9. As clearly shown in Figure 3, the rate of the photodegradation process of PCBs is dependent on the pH values. When the pH value was 5, a rapid degradation process for PCBs with the highest degradation rate (0.3742 min^{-1}) was obtained. This value is 2.26 times higher than that obtained at pH 9. Generally, the mechanism of the photocatalytic degradation reaction using TiO_2 as a photocatalyst depends on the adsorption between the target compound and the photocatalyst. The extent of such adsorption depends on the charge of the degraded compound as well as the catalyst, which in turn depends on the pH of a given solution. At pH value lower than the point of zero charge (pH_{pzc}) of TiO_2, positively charged TiO_2 surface with the species $TiOH_2^+$ exists, while the PCBs and intermediates are negatively charged naturally. Consequently, the adsorption of PCBs is favorable at low pH due to the electrostatic attraction. Furthermore, formation of carbonate ions, which are effective scavengers of hydroxyl radical ($^{\bullet}OH$), is favorable at high pH values; as a result, reduction of the degradation efficiency was observed.

3.2.3. Photocatalytic Activity of n-TiO_2 and CM-n-TiO_2. In order to examine the photocatalytic efficiency of CM-n-TiO_2, comparison with unmodified n-TiO_2 was performed under

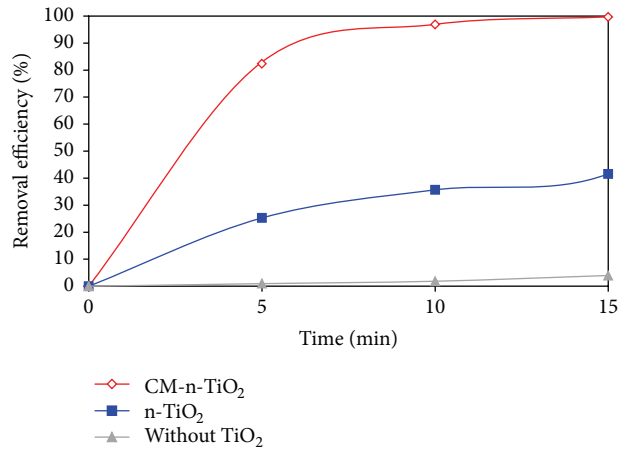

Figure 4: Photocatalytic degradation of a mixture of Ar 1254 (0.5 ppm) and Ar 1260 (0.5 ppm) in seawater using n-TiO_2 and CM-n-TiO_2 under illumination of UV light.

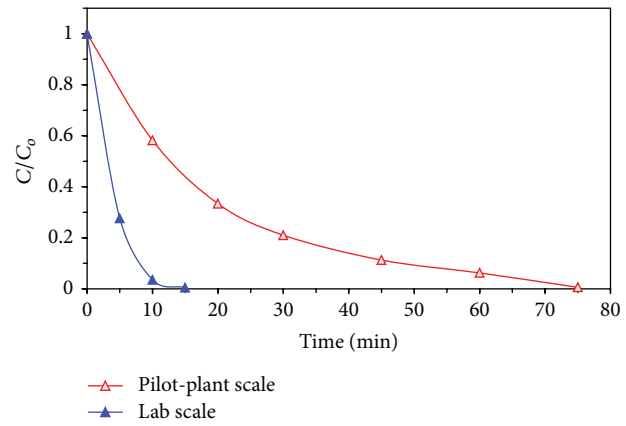

Figure 5: Photocatalytic degradation of PCBs (1.0 ppm) in seawater using CM-n-TiO_2 at lab scale and pilot-plant scale.

the same optimum experimental conditions (Figure 4). No degradation was obtained in the absence of the photocatalyst (i.e., under photolysis conditions). The photocatalytic efficiency of CM-n-TiO_2 (0.5 g L^{-1}) towards the photocatalytic degradation of mixture of Ar 1254 (0.5 ppm) and Ar 1260 (0.5 ppm) in seawater at the optimum pH 5 under illumination of UV light is much higher than that of n-TiO_2. Complete degradation of PCBs was achieved after 15 min of UV light illumination. On the other hand, when the reference TiO_2 was used, only 45.92% of the same concentration of PCBs was removed after the same irradiation period. The remarkable enhancement in the photocatalytic activity of CM-n-TiO_2 nanoparticles can be attributed to the narrowing of the optical bandgap energy from 2.99 eV for n-TiO_2 to 1.8 eV for CM-n-TiO_2 as a result of the carbon modification of TiO_2 [4–6, 9]. The significant narrowing of the optical bandgap energy of CM-n-TiO_2 can be ascribed to the mixing of C 2p with the O 2p valence bands [20] as a result of the carbon modification of titanium oxide. The observed optical behavior of the low bandgap energy for the synthesized CM-n-TiO_2 is in good agreement with the previously reported E_g values of 2.35 eV [4], 1.45 eV [5], and 1.86 eV [6]. Furthermore, theoretical studies by Di Valentin et al. [21] addressed the notion that the presence of interstitial and substitutional carbon dopants incorporated into TiO_2 drastically lowered its bandgap. Nie and Sohlberg [22] obtained low bandgap value of 2.32 eV by incorporation of carbon into n-TiO_2 and predicted the possibility of achieving low bandgap of 1.58 eV by some complex carbon incorporation.

3.3. Photocatalytic Degradation at Pilot-Plant Scale. To evaluate the viability and the performance of the solar pilot plant (SFFR), the photocatalytic degradation of PCBs (1.0 ppm) in seawater was examined at the optimal conditions, obtained from laboratory scale experiments, of pH 5 and 0.5 g L^{-1} of CM-n-TiO_2 (Figure 5). Complete degradation of PCBs was achieved after 15 and 75 min of irradiation under UV (lab scale) and sunlight (pilot plant), respectively. It is clearly noted that the remediation of PCBs at lab scale under UV light for 500 mL sample was successfully extrapolated to a larger pilot-plant system for 20 L of polluted seawater under illumination of real sunlight.

On the other hand, a comparison with regular n-TiO_2 was performed under the same experimental conditions in order to assess the photocatalytic performance of CM-n-TiO_2 in the SFFR for the degradation of Ar 1254 (0.5 ppm), Ar 1260 (0.5 ppm), and a mixture of Ar 1254 (0.5 ppm) and Ar 1260 (0.5 ppm). As a result of carbon incorporation, remarkably higher photodegradation efficiency of CM-n-TiO_2 is clearly noted, reflecting the capability of CM-n-TiO_2 to harvest maximum solar light photons and hence enhance the degradation efficiency. After 60 min of solar irradiation, PCBs were easily degraded with efficiencies of 92.1% for Ar 1254 (Figure 6(a)), 94.6% for Ar 1260 (Figure 6(b)), and 93.7% for the mixture of Ar 1254 and Ar 1260 (Figure 6(c)).

3.4. Kinetic Studies. To depict the kinetics of photocatalytic reactions of aqueous organics, the Langmuir-Hinshelwood (L-H) model was employed [23–25]. According to this model, the relationship between the degradation rate (r) and concentration of the reactant in water at time t (C) can be expressed as follows:

$$r = -\frac{dc}{dt} = \frac{k_r K_{\text{ad}}}{1 + K_{\text{ad}} C}, \tag{2}$$

where the constants k_r and K_{ad} represent the rate and the adsorption equilibrium, respectively. This equation can be simplified to represent the pseudo-first-order reaction when C_o is very small as follows:

$$\ln\left(\frac{C_o}{C}\right) = k_r K_{\text{ad}} t = k_{\text{app}} t, \tag{3}$$

where k_{app} and C_o are the apparent first-order rate constant and the concentration at zero time, respectively. The half-life time reaction ($t_{1/2}$), the amount of time required for 50% of

Table 2: Apparent rate constants (k_{app}) and half-life time reaction ($t_{1/2}$) for the photocatalytic degradation of PCBs in seawater using the pilot plant (SFFR).

PCBs	CM-n-TiO_2			n-TiO_2		
	k_{app} (min^{-1})	$t_{1/2}$ (min)	R^2	k_{app} (min^{-1})	$t_{1/2}$ (min)	R^2
Ar 1254 (0.5 ppm)	0.0416	16.66	0.9854	0.0218	31.80	0.9759
Ar 1260 (0.5 ppm)	0.0509	13.62	0.9818	0.0231	30.01	0.985
Ar 1254 (0.5 ppm) + Ar 1260 (0.5 ppm)	0.0482	14.38	0.9909	0.0225	30.81	0.9983

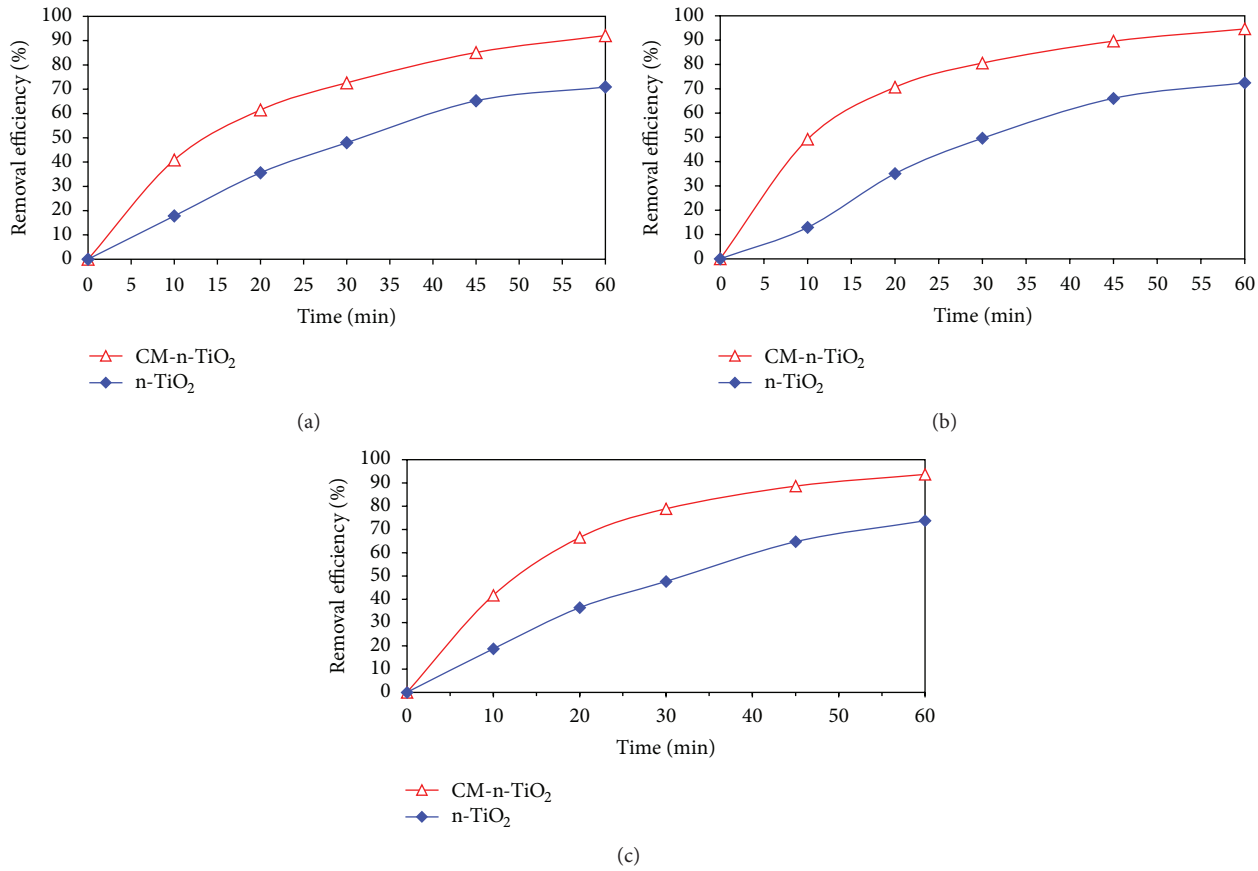

Figure 6: Photocatalytic degradation of (a) Ar 1254 (0.5 ppm), (b) Ar 1260 (0.5 ppm), and (c) mixture of Ar 1254 (0.5 ppm) and Ar 1260 (0.5 ppm) in seawater at the optimal conditions of pH 5 and 0.5 g L^{-1} of the photocatalyst (n-TiO_2 and CM-n-TiO_2) under illumination of natural sunlight using the pilot plant (SFFR).

the initial concentration to disappear, can be calculated as follows:

$$t_{1/2} = \frac{\ln(2)}{k_{app}}. \quad (4)$$

By plotting $\ln(C_o/C)$ versus irradiation time (t), a linear behavior that indicates pseudo-first-order kinetics for the photocatalytic degradation of PCBs was obtained (Figure 7). From the apparent rate constant, calculated from the slope of the linear plot, and $t_{1/2}$ values (Table 2), it is interesting to note that the solar photocatalytic degradation of PCBs using the pilot plant (SFFR) in the presence of CM-n-TiO_2 is twofold faster in comparison with that of regular TiO_2, confirming the potentiality of CM-n-TiO_2/SFFR as an efficient system for the photocatalytic degradation of PCBs in seawater.

4. Conclusions

Unique carbon-modified titanium oxide (CM-n-TiO_2) nanoparticles were successfully fabricated via sonicated sol-gel method using titanium(IV) isopropoxide as Ti and a carbon-containing precursor. Comparative evaluation of the photocatalytic performance of carbon-modified and regular titanium oxide towards the photocatalytic removal of PCBs was performed. The bandgap energy has been reduced from 2.99 eV for n-TiO_2 to 1.8 eV for CM-n-TiO_2, which in turn improved the photocatalytic performance of CM-n-TiO_2 by absorption of more light photons. The results showed that the removal rate of PCBs was favorable at catalyst dosage of 0.5 g L^{-1} and pH 5. The photodegradation kinetics of PCBs using CM-n-TiO_2 followed a pseudo-first-order reaction.

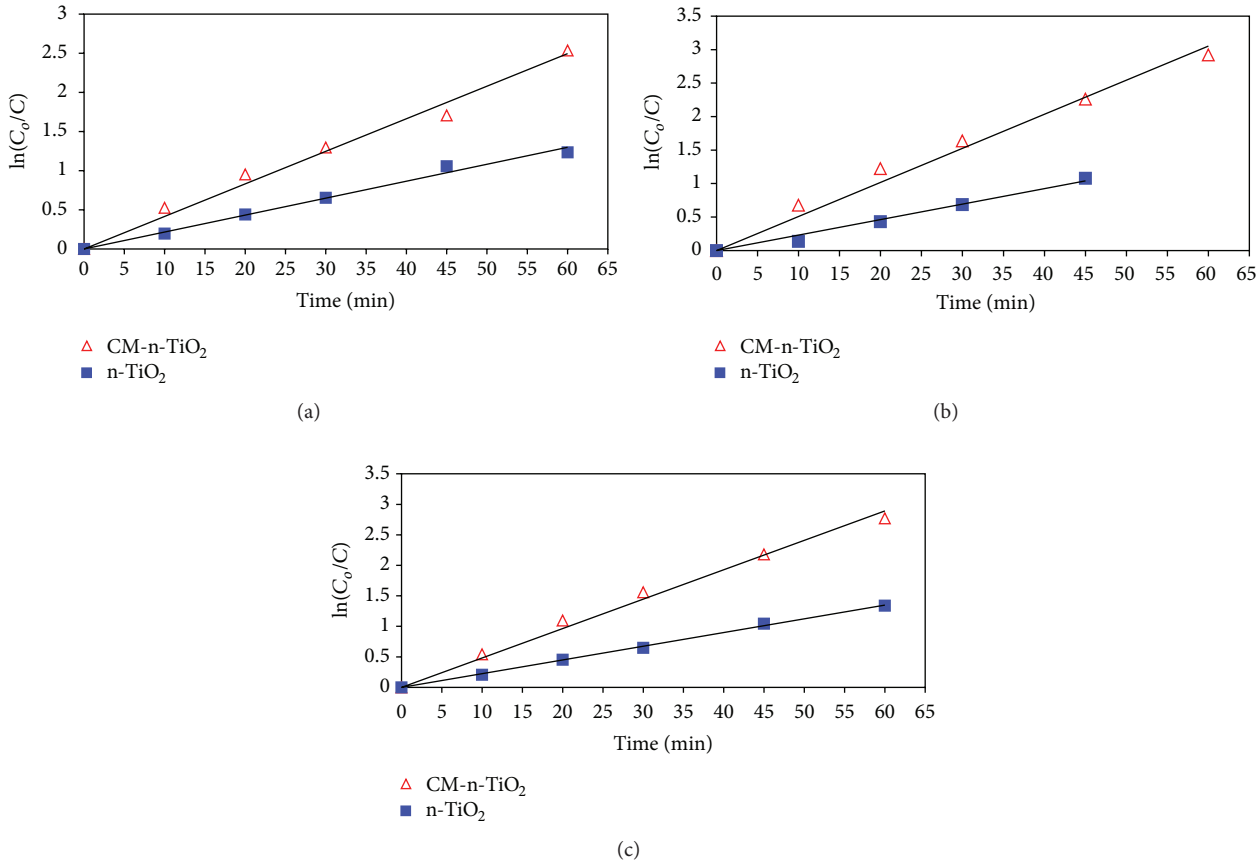

FIGURE 7: Kinetic analysis for the photocatalytic degradation of (a) Ar 1254 (0.5 ppm), (b) Ar 1260 (0.5 ppm), and (c) mixture of Ar 1254 (0.5 ppm) and Ar 1260 (0.5 ppm) in seawater using the pilot plant (SFFR).

The photocatalytic degradation of PCBs in seawater has been successfully achieved using CM-n-TiO_2 nanoparticles at laboratory level with UV light and at pilot-plant scale (SFFR) under natural solar radiation. Furthermore, the results obtained evidenced the validity of CM-n-TiO_2/SFFR system as an attractive and promising technique for the remediation of polluted water.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

This project was funded by the National Plan for Science, Technology and Innovation (MAARIFAH), King Abdulaziz City for Science and Technology, Kingdom of Saudi Arabia, Award no. 12-NAN2241-03. The authors also acknowledge with thanks the Science and Technology Unit, King Abdulaziz University, for technical support. The authors are thankful to Mr. Kazem Sultan and Mr. Yasar N. K. for their appreciable help in the experimental analysis.

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