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COD reduction by TiO_2/graphene photocatalytic treatment of ethylene dichloride in wastewater

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ABSTRACT

Photocatalytic degradation of ethylene dichloride (EDC) wastewater was investigated in a batch photocatalytic reactor using titanium dioxide (TiO_2)/graphene hybrid as the catalyst for the first time. The main advantage of this structure, in which graphene was used as a bed for TiO_2, was that it enhanced the electron transfer considerably. The degradation in the organic waste was evaluated in terms of chemical oxygen demand (COD). The concentration of EDC, the amount of the photocatalyst, the concentration of graphene in the catalyst structure, and the pH of the solution were found effective in reaction efficiency. For an initial EDC concentration of 750 ppm, the optimum conditions for EDC removal from the wastewater were 2 g/l concentration of photocatalyst concentration, 1 wt% concentration of graphene in the hybrid structure, and a pH of 4. The experiments were carried out at 5°C. It was found that using this structure, only 4 h of treatment was sufficient to obtain a considerable COD reduction. Increasing irradiation intensity from 100 to 200 W increased EDC removal from 69.1 to 81.8%.

Keywords: Wastewater; Photocatalytic; COD; Graphene; TiO_2 nanoparticles; UV

1. Introduction

Chlorinated hydrocarbons such as ethylene dichloride (EDC) are the main pollutants found in the wastewater of the petrochemical industry [1]. The quantity and characteristics of the wastewater generated depend on the process configuration. Use of photo-oxidation reactions is very useful since the role of sunlight in modifying organic compounds in the environment has been recognized [2]. Hence, in the recent years, considerable attention has been paid to the advanced oxidation processes (AOPs) [3]. Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst as an AOP. This reaction is based on radiations with wavelengths close to those of sunlight's [4]. Hence, removing chlorinated hydrocarbon pollutants from output wastewater was often done by using photocatalytic oxidation [5]. This process is highly dependent on the *in situ* generation of hydroxyl radicals [6]. Using photocatalytic oxidation in sewage treatment has been investigated [7]. All of these experiments have shown high efficiencies in the degradation and removal of pollutants from water and sewage by this method [8,9]. It is an effective, fast, efficient, and eco-friendly method for wastewater treatment.

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Semiconductors are primary light absorbers [10] and are used in photocatalysis because of their light absorption properties [11]. Titanium dioxide (TiO_2), as a metal chalcogenide semiconductor, is one of the effective photocatalysts due to its chemical inertness and photostability in the near UV band energy gap [12]. The electrons in graphene generally behave like mass less particles [13]. In the graphene super lattices; however, the electrons behave as though they have acquired mass, similar to neutrinos [14].

The activity of TiO_2 can be enhanced by combination with other semiconductors, such as graphene, as a catalyst improver [15]. In this work, TiO_2 was hybridized with graphene for photodegradation of aqueous EDC. The effects of the independent variables influencing the efficiency of the photocatalytic reaction, including the concentration of EDC in water (ppm), the concentration of graphene (%) in the hybrid structure, photocatalyst amount (g/l), and the pH of the solution were studied. Taguchi method was applied to the modeling and optimization of EDC degradation in wastewater [16]. In addition, chemical oxygen demand (COD) removal was monitored in order to explain the mineralization of EDC in the photocatalytic process [17]. Finally, the effect of the duration and the light intensity of UV irradiation were assessed for optimum condition.

2. Experimental

2.1. Materials

Graphene powder with few-layered structure was purchased from Graphenea Spanish CO., which was synthesized on a copper substrate by the CVD process [18]. Titanium butoxide as the titanium precursor of TiO_2 was purchased from Sigma Aldrich. HNO_3, H_2SO_4, isopropanol, and ethylene glycol from Merck were used in this work. EDC (99.5% purity) supplied by Bandar Imam Petrochemical Complex (Iran) was used for making the reacting solution.

2.2. Photoreactor setup

A batch reactor system, comprised of a 500 ml double wall Pyrex beaker as the reactor and two NEC UV lamps (50 Hz) as the UV light source, was used for treatment of the wastewater. The intensity of the UV light by each lamp is 100 W. The highest irradiation peak of the UV lamps was at 250–320 nm (measured with a TOPCON UV-R-1 spectroradiometer). The UV lamps were placed at the center of the reactor located inside quartz tubes as an artificial light source to provide near UV radiation. The tubes were made of quartz to achieve the maximum possible light utilization, as UV light cannot pass through glass and Pyrex. Therefore, the maximum light utilization was achieved. A DC power supply (TM.ECHNI 245, Italy) was used in the experimental setup.

A lab-scale air pump was located below the reactor and provided an adjustable circulating stream for proper mixing and fluidizing of catalyst nanoparticles inside the reactor. Airflow was supplied to the reactor at a constant flow rate of 2.1 l/min. The reactions were performed at 5℃, adjusted by a circulator. Each experiment was carried out for 4 h, under different initial pHs of 4, 7, and 10. A schematic diagram of the experimental setup is depicted in Fig. 1.

2.3. Synthesis of TiO_2/graphene photocatalyst

The graphene sheets had to be treated with a strong acid, first. For this purpose, 0.6 g of graphene was added to 160 ml of a 1:3 (v/v) mixture of concentrated HNO_3–H_2SO_4, followed by constant stirring at 60℃ for 180 min [19]. The mixture was then centrifuged and washed with distilled water until the pH reached 7. Subsequently, the pretreated graphene was dried in an oven at 65℃ for 3 h.

A successful method for the attachment of TiO_2 to functionalized graphene explained in the following. The desired amount of functionalized graphene was dispersed in 40 ml of an aqueous solution [pH 1.5 (adjusted with HNO_3)] by ultra sonication for 30 min at ambient temperature. Next, 1 ml of titanium butoxide and 20 ml of isopropanol were slowly added to the suspension dropwise. Then 1.5 ml of ethylene glycol was added and the mixture was stirred at 80℃ for 10 h. The resulting mixture was magnetically stirred under N_2 atmosphere. The dark precipitates were separated from the solution by high-speed centrifugation (14,000 rpm), resuspended in isopropanol (10 ml × 3) and centrifugeed until the

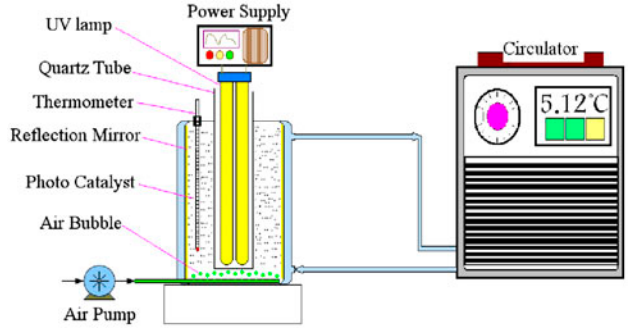

Fig. 1. A schematic diagram of the photoreactor setup.

supernatant became colorless and the organic species were removed. The collected materials were left to dry in an oven at 65°C for 12 h. Finally, the powder was calcinated at 300°C for 2 h to obtain the TiO_2/graphene hybrid nanostructures [20]. The sample was assigned as TiO_2/graphene hybrid at different weight ratios of graphene to TiO_2.

2.3.1. TEM imaging

Fig. 2 is a TEM micrograph showing TiO_2/graphene hybrid structure, grown at 80°C under N_2. This attractive observation shows that TiO_2 particles are connected to the graphene film. In addition, the good dispersion of TiO_2 in the hybrid structure can be clearly seen.

2.4. Experimental design and procedures

The photocatalytic degradation of EDC was evaluated by monitoring the reduction of carbon content in the wastewater after the process. To find the optimum conditions for economic removal of the pollutant from the wastewater, 3 levels of each variable (low, medium, and high) were studied. Table 1 presents the variables along with their corresponding levels in the design of experiments by Taguchi method. The pH of the solution is a significant variable in the evaluation of aqueous phase mediated photocatalytic reactions.

Solutions containing 750, 1,750, and 2,750 ppm of EDC in pure water were prepared as the wastewater. The pH of each solution was adjusted with dilute NaOH at three levels of 4, 7, and 10. Then, 1.5, 2.0, and 2.5 g/l of photocatalysts were added to each of the solution separately. After preparation, 240 cc of each solution was poured into the reactor separately.

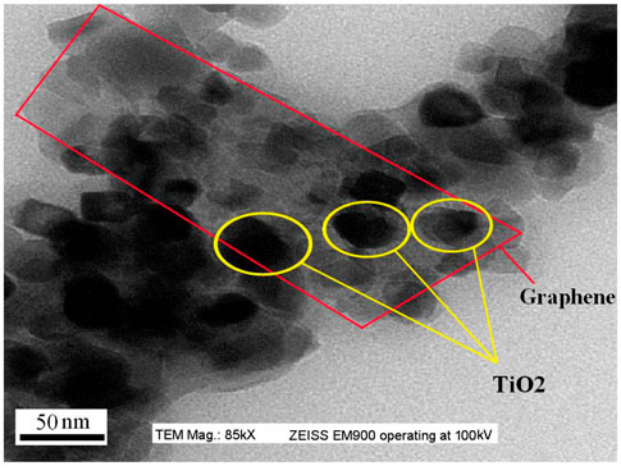

Fig. 2. TEM image of the TiO_2/graphene hybrid.

Temperature is one of the parameters affecting photocatalysis [7]. Due to high volatility of EDC, large amounts of it would vaporize from the solution at ambient temperature. Therefore, the reactions were done at a constant temperature of 5°C set by a circulator. The solution was mixed with the photocatalyst in a dark environment for 30 min in order to measure the amount of EDC absorption through the photocatalytic reaction. Subsequently, the reaction took place under the radiation of UV lamps for 4 h. To keep the suspension homogeneous, stirring and aeration were maintained. The COD of the wastewater was measured before and after the reaction, using a Palintest 7200 photometer. The amount of the EDC consumed is proportional to the COD of the wastewater sample. Based on the COD results, the photocatalytic degradation efficiency (η) was calculated using the following equation:

$$\eta = (COD_1 - COD_2)/COD_1 \times 100 \quad (1)$$

3. Results and discussion

3.1. Effects of independent variables by design of experiments

As with most processing techniques, several variables affect the performance of photocatalytic degradation. Various variables, each at three different levels, necessitate design of experiments by Taguchi method. Design Expert 8® software was employed to decrease the number of experiments to 9 for obtaining the optimum conditions. The results of the designed experiments and the theme results are shown in Table 2.

According to Table 2, photocatalytic degradation of EDC significantly enhanced by increasing the amount of photocatalyst and the concentration of graphene in the hybrid structure. This is due to the fact that higher loads of the photocatalyst in the solution lead to enhanced light adsorption as well as increased light penetration through the aqueous medium.

The photocatalytic degradation efficiency decreased considerably with increasing the pH of the solution from 7 to 10. It showed lower degradation efficiency at neutral pH than at acidic condition. The photocatalytic degradation efficiency was considerably decreased when the concentration of EDC increased in the water. This lowered efficiency was due to increased scattering of light and its lower transmission through the wastewater.

Table 1
The levels of the photocatalytic process variables

Independent variable	Low level	Medium level	High level
EDC conc. (ppm)	750	1,750	2,750
Graphene conc. in catalyst (%)	0.5	1	1.5
Photocatalyst amount (g/l)	1.5	2	2.5
pH	4	7	10

Table 2
Condition of designed experiments by Taguchi method

	Independent variables				Response		
Experiments	EDC conc. (ppm)	Graphene conc. (%)	Photocatalyst (g/l)	pH	COD_1 (mg/l)	COD_2 (mg/l)	COD reduction (%)
1	750	0.5	1.5	4	434.9	94.8	78.2
2	750	1	2	7	434.9	87.4	79.9
3	750	1.5	2.5	10	434.9	108.3	75.1
4	1,750	0.5	2	10	824.5	183.0	77.8
5	1,750	1	2.5	4	824.5	186.3	77.4
6	1,750	1.5	1.5	7	824.5	194.6	76.4
7	2,750	0.5	2.5	7	1,134.1	280.1	75.3
8	2,750	1	1.5	10	1,134.1	271.0	76.1
9	2,750	1.5	2	4	1,134.1	259.7	77.1

3.2. Effects of irradiation time and intensity on COD removals

Having determined the optimum conditions, the effects of irradiation time and intensity (only the results presented here) on COD removal were investigated under these conditions. Fig. 3 shows COD reduction with time, as measured from the samples taken from the solution at different times under optimal conditions.

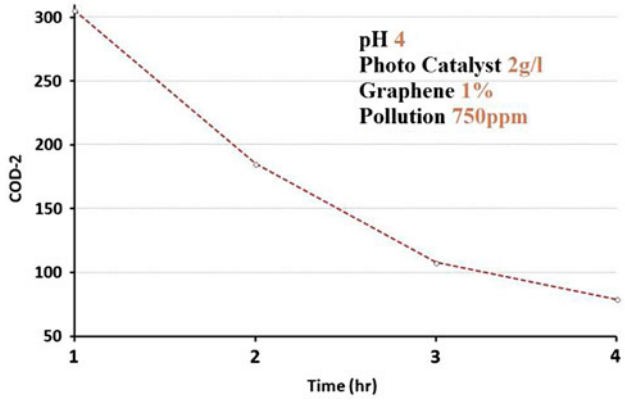

Fig. 3. COD decreasing over time under the optimum conditions.

As it can be seen in Fig. 3, major reductions in COD can be achieved in relatively short time periods. For example, COD reduced by 75.2 and 81.8% after 3 and 4 h, respectively. However, there was little change in the COD after this point, showing that the best time to remove a sufficient amount of EDC was 4 h. In a similar work, Nikazar et al. [7] investigated the photocatalytic degradation of EDC in water using a TiO_2/Clinoptilolite photocatalyst combined with H_2O_2 treatment. In their study, the highest efficiency achieved with optimized parameters was 74%. Similar results have also been reported [21,22]. Therefore, the method employed in this work is superior in terms of COD removal, i.e. photocatalytic degradation. Thus, hybridizing TiO_2 with graphene is suggested as a promising method of photocatalytic wastewater treatment.

To evaluate the effect of UV light intensity on the efficiency of the photocatalytic reaction, two intensities, i.e. 100 and 200 W were studied. It was seen that increasing irradiation intensity improved EDC removal by about 12.7%.

4. Conclusion

In this work, we reported the use of TiO_2/graphene hybrid structure as the photocatalyst for the photodegradation of EDC in water in a batch photoreactor. Design of experiments was carried out using Taguchi method to obtain the optimum conditions of photodegradation. In order to achieve the highest efficiency according to the experimental values obtained by Taguchi method: the best concentration of graphene in the catalyst was 1 wt%,

(1) the best amount of the photocatalyst in the wastewater was 2 g/l,
(2) the pH of solution should be 4 (acidic range),
(3) and the best EDC concentration was 750 ppm.

Maximum efficiency of 81.8% for photocatalytic degradation of EDC was obtained after just 4 h with the optimized parameters. This was promisingly higher compared to similar works, suggesting the hybrid structure as a suitable photocatalyst. Increasing EDC concentration above 750 ppm caused increasing turbidity of the solution and delayed further penetration of light into the reactor, thereby reducing the efficiency. The photo-biodegradation proved effective in removing EDC from the wastewater. The best irradiation time was 4 h and EDC removal increased by increasing UV irradiation intensity. The treated wastewater may be recycled for use in the same industry or for other applications like agriculture, where water of a lower quality may still be satisfactory.

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