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Photocatalytic Degradation of Ethylene Dichloride in Water Using Nano TiO_2 Supported on Clinoptilolite as a Photocatalyst

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ABSTRACT

In this article one of the advanced oxidation processes (AOP) combined methods, photocatalyst /H_2O_2, is utilized in order to study photodegradation of ethylene dichloride (EDC) in water. Nano Titanium (IV) Oxide, supported on Clinoptilolite (CP) (Iranian natural zeolite) using solid-state dispersion (SSD) method for improvement of its photocatalytic properties. The results show that the TiO_2/Clinoptilolite (SSD) is an active photocatalyst. The effects of five important photocatalytic reaction parameters including the initial concentration of ethylene dichloride, the ratio of TiO2/Clinoptilolite, the catalyst concentration, H2O2 concentration and pH in photodegradation of ethylene dichloride were examined. In this experiments, the design and also the optimum parameters were obtained by Taguchi Method, using Design Expert8® software. Taguchi's L27 (5^3) orthogonal array design was employed for the experimental plan. Four parameters were found to be significant whereas, pH was found to be an insignificant parameter after conducting experiments. A first order reaction with K = 0.007 min-1 was observed for the photocatalytic degradation reaction.

Keywords: Photodegradation; Photocatalysts; TiO_2/Clinoptilolite; Ethylene Dichloride

1. Introduction

Effects of several different pollutions such as phenol compounds, alcohols, organic acids, hydro-carbonic sulfur compounds, pesticides and insecticides compounds, dyes, output wastewater from various industries and etc. using photocatalytic oxidation has been investigated on sewage treatment. All of these experiments show high efficiency in degradation and removal of these pollutions from water and sewage by this method [1,2]. Usual biological treatment methods for hazardous compounds such as chlorinated hydrocarbons are not efficient, because of high toxicity of these compounds which results in destroying microorganisms. TiO_2 is one of the most effective photocatalysts due to its biological and chemical inertness and photo stability in near- UV band energy gap, and can be used as a fine powder or crystals dispersed in water and wastewater treatment applications. However, the need to filter TiO_2 particles after reaction makes such a process troublesome and costly. Thus, in order to solve this problem, many researchers have examined several methods for fixing TiO_2 on supporting materials including glass beads [3-5], fiber glass [6-8], silica [9,10], and zeolite [11,12]. When using zeolite as TiO_2 support, care should be taken that TiO_2 does not lose its photo activity and the adsorption properties of zeolite are not affected. Matthews [4] showed that the photo efficiency of TiO_2 is suppressed when TiO_2 is in interaction with the zeolite.

In this work TiO_2 was supported on a zeolite without losing photo efficiency and affecting the adsorption properties of zeolite using the exact method suggested by Nikazar et. al. [13] for supporting TiO_2 on Clinoptilolite. This mixture was used for photodegradation of aqueous EDC.

2. Experimental

2.1. Materials

Degussa P-25 titanium dioxide with a crystallographic mode of 80% anatase and 20% rutile, a 50 m^2g^{-1} BET surface area and an average particle size of 30 nm (according to the manufacturer's specifications) and the raw material was an Iranian commercial Clinoptilolite (CP) (Afrand Tuska, Iran) from deposits in the region of Semnan. According to the supplier's specifications, it contains about 90 wt% CP (based on XRD internal standard quantitative analysis) and the Si/Al molar ratio is 5.78. The concentration of Fe_2O_3, TiO_2, MnO and P_2O_5 impurities has been reported to be 1.30, 0.30, 0.04 and 0.01 wt% respectively, and were used for preparation of the photocatalyst. Merck H_2O_2 with 30% purity, and Ethylene dichloride (EDC) produced by Bandar Imam Petrochemical Comlex, with 96% purity for making reacting solution.

2.2. Preparation of TiO_2-supported on CP Catalysts

The Solid State Dispersion (SSD) method was applied for supporting photocatalyst on zeolite. In this method, nano titanium peroxide was mixed with CP using ethanol as a solvent and mixture was grinded for 3 hours. Ethanol was then removed by evaporation. Samples were dried at 110°C in the oven and calcined at 450°C in the furnace for 5 hours to obtain TiO_2-supported zeolite photocatalysts [13].

2.3. Apparatus

Photocatalytic reaction was performed in a batch Pyrex double

wall reactor of 1.5 L in volume with two 8-W UV-C mercury lamps located in quartz tubes inside the reactor. The tubes were made from quartz because UV-C light cannot pass through glass and Pyrex.The photo reactor used in this experiment is shown in **Figure 1**. Circulator has been used for temperature adjustment and GC VARIAN CP-3800 was used for EDC concentration measurement.

2.4. Procedures

A solution containing known concentration of EDC was prepared; subsequently 800 cc of this solution was poured into the reactor. The solution pH value was adjusted at desired level using dilute NaOH and H_2SO_4. Then certain amount of prepared photocatalyst and H_2O_2 was added to the solution. Photocatalytic reaction took place under the radiation of mercury lamps while agitation and aeration was maintained to keep the suspension homogeneous and oxygenized. Sampling was performed at specified times and concentration of EDC was determined using GC.

3. Design of Experiments

Effects of five parameters that influence the efficiency of photocatalytic reaction have been studied in these experiments. Initial concentration of pollutant (EDC), H_2O_2 concentration, catalyst amount, TiO_2% and pH, each of them in three levels, are shown in **Table 1**.

Because of numerous studying parameters, each at 3 different levels, Taguchi method for design of experiments using Design Expert 8.0.5® was employed to decrease the number of experiments to 27 for obtaining optimum terms. Temperature is one of the effective parameters on photocatalytic reactions that are usually set at ambient temperature, but due to high volatility of ethylene dichloride in the ambient temperature and aeration during process, large amount of EDC would be vaporized from the solution. Therefore, reaction's temperature was set at 5°C using circulator.

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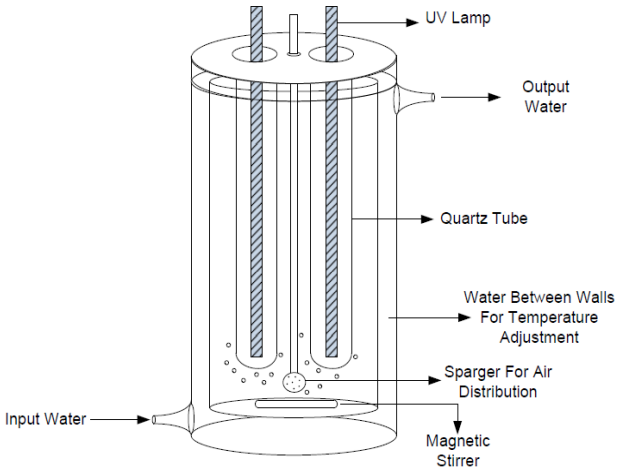

Figure 1. Schematic of photo reactor.

Table 1. Experimental parameters and their levels.

Process Parameters		Level 1	Level 2	Level 3
Catalyst Concentration g/L	A	0.1	0.25	0.5
H_2O_2 Concentration (ppm)	B	0	50	100
Initial Concentration of EDC (ppm)	C	200	400	600
pH	D	4	7	10
TiO_2%	E	10	15	20

4. Results and Discussion

4.1. Taguchi Method

ANOVA analysis is shown in the **Table 2**.

SUM of Squares: sum the squared differences between the average values for the blocks and the overall mean.

DF: degrees of freedom attributed to the blocks, generally equal to one less than the number of blocks.

Mean square: estimate of the block variance, calculated by the bock sum of squares divided by block degrees of freedom.

The F-value of 33.10 implies the model is significant Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, E are significant model terms.

In the **Figure 2** we can see a graph of the predicted response

Table 2. ANOVA analysis report.

Source	Sum of Squares	DF	Mean Square	F Value	Prob. > F
Model	52.27853	8	6.5348162	33.101924	$< 10^{-4}$
A-[Catal]	10.67263	2	5.336314	27.030945	$< 10^{-4}$
B-[H_2O_2]	4.036541	2	2.0182704	10.223491	0.0011
C-[EDC]$_0$	31.69998	2	15.849991	80.287672	$< 10^{-4}$
E-TiO_2%	5.86938	2	2.9346898	14.865587	0.0002
Residual	3.55347	18	0.197415		
Cor Total	55.832	26			

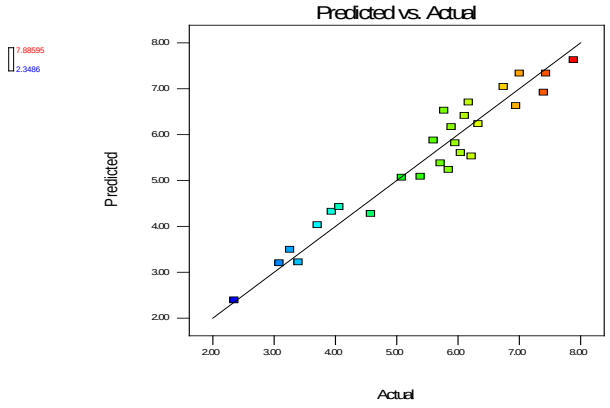

Figure 2. Predicted vs. Actual plot.

values versus the actual response values. It is clear that all of the values are predicted by the model.

Responses should be assigned as "larger is better" for enhancing optimized parameters as showed below:

[Catal]	$[H_2O_2]$	$[EDC]_0$	pH	TiO_2%	R_1	Desirability
0.25	50	200	7	15	0.739634	1

4.2. Kinetics of Photocatalytic Degradation of EDC

Several experimental results indicated that the degradation rates of photocatalytic oxidation over illuminated TiO_2 fitted by the first-order kinetic model [14-16]. **Figure 3** shows the plot of $\ln([EDC]_0/[EDC])$ vs. irradiation time for EDC. The linearity of plot suggests that the photodegradation reaction approximately follows the pseudo-first order kinetics with K = 0.007 min^{-1}.

4.3. Effects of UV Irradiation and Photocatalyst Ingredient

In **Figure 4** the comparison of four experiments is shown. First column is degradation efficiency of EDC using only UV light without photocatalyst, this column shows the importance of photocatalyst because eliminating photocatalyst from reaction caused decrease in efficiency about 47%. Second column is about degradation efficiency of EDC employing 15% wt TiO_2 photocatalyst without UV irradiation, this column shows influence of UV light in activating photocatalyst, reaction efficiency with elimination of UV light cause 45% efficiency reduction. Third column is shown degradation efficiency of EDC using pure TiO_2 (degussa P25 without zeolite) catalyst with UV irradiation, supporting catalyst on zeolite increase reaction efficiency about 37%. In last column degradation efficiency of EDC with optimum parameters has been brought for comparison. All of the other parameters are the same.

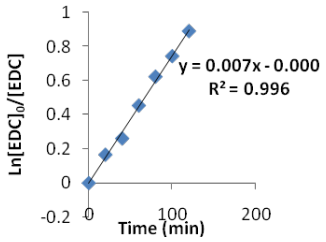

Figure 3. Plot of reciprocal of pseudo-first order rate constant against initial concentration of EDC = 200 ppm, concentration of photocatalyst (15 wt% TiO2/CP) = 0.25 g/L, $[H_2O_2]$=50 ppm, T = 278 K, pH = 7.

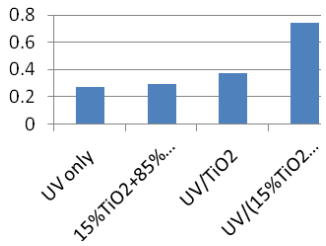

Figure 4. Comparison of degradation efficiency in four different experiment in T= 278 K, pH=7, $[H_2O_2]$=50 ppm, $[EDC]_0$=200 ppm, [catalyst]=0.25 g/L.

5. Conclusion

1. SSD method is an effective method for supporting TiO_2 on Clinoptololite.
2. The following optimum terms obtained with Taguchi method :

Initial concentration of EDC 200 ppm, catalyst concentration 0.25 g/L, H_2O_2 concentration 50 ppm, TiO_2% 15 and effect of pH and two parameters interactions were not significant enough.

3. Initial concentration of EDC, Catalyst concentration, TiO_2% and H_2O_2 concentration were effective in reaction efficiency, respectively.
4. Maximum efficiency of 74% for photocatalytic degradation of EDC was obtained with optimized parameters.
5. The kinetic of photocatalytic degradation of EDC is of the pseudo-first order with K = 0.007 min^{-1}.

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