

Application of a Novel Nanocomposite for Desulfurization of a Typical Organo Sulfur Compound

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ABSTRACT: In this research, zeolite-TiO₂ nanocomposite was prepared for degradation of dibenzothiophene as a typical aromatic organosulfur compound of transportation fuels. The synthesized TiO₂ was immobilized on the surface of clinoptilolite by Solid State Dispersion (SSD) method. The nanocomposite was then characterized by XRD, FTIR, TEM and SEM techniques. Photodegradation of dibenzothiophene in n-hexane solution by the prepared photocatalyst was then studied under different experimental conditions. The reaction products were identified by GC and GC-MS techniques. The removal of degradation products from the solution was examined by β -zeolite. The results showed that under optimized conditions, the photocatalyst was able to degrade %88 of dibenzothiophene and that the degradation products were adsorbed by β -zeolite so that the remaining solution was deeply desulfurized. It was also concluded that the kinetics of the reaction was first order.

KEY WORDS: Desulfurization, Dibenzothiophene, β -zeolite, Clinoptilolite, Nanocomposite.

INTRODUCTION

Sulfur compounds in the exhaust gases of diesel engines cause formation of acid rain, photochemical smog, and sulfate particulate matter, which pollute the environment and endanger public health [1,3]. In many countries new environmental legislations have been established and the average sulfur content has been restricted to 10 μ g/mL, even the zero level in the near future [4,5]. Hydrodesulphurization (HDS) as the most used technique is able to desulfurize aliphatic and acyclic sulfur-containing compounds effectively but dibenzothiophene which is a typical aromatic organosulfur compound can not be easily removed by HDS technique. Furthermore operation at high temperatures

and high hydrogen pressures creates many problems, including high investment, high operating cost, and reduction of the length of the catalyst cycle [6-10]. The oxidative desulfurization (ODS) has received much attention as an alternative technology for deep desulfurization of oils because of its attractive feature, including lower temperature, mild pressure conditions, and useless hydrogen [11-12]. Titanium dioxide (TiO₂) is one of the most popular and promising materials in photocatalytic application due to its strong oxidizing power, high photostability and redox selectivity. An important requirement for improving the TiO₂ catalytic activity is to increase its specific surface area,

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but the recycling difficulties restricted the utilization of finer TiO_2 particles. Thus, in practical applications, TiO_2 nanoparticles have been considered to be fixed on the surface of inert and special supports. Among various supporting materials, zeolites seem as attractive candidates due to their unique uniform pores, super adsorption capability and special ion-exchange ability [13-19]. Clinoptilolite is the most common and widely distributed natural zeolite with a two-dimensional layer-like structure in which $(\text{Si}, \text{Al})\text{O}_4$ tetrahedral are linked through oxygen atoms in layers [20]. In this work, we report a photocatalytic oxidation system using TiO_2 -clinoptilolite as photocatalyst for degradation of dibenzothiophene. Then the removal of sulfur-containing photodegradation products by β -zeolite is reported.

EXPERIMENTAL SECTION

Materials and apparatus

Dibenzothiophene, n-hexane and titanium isopropoxide were purchased from Merck company and were in analytical grade. Natural clinoptilolite was obtained from deposits of Semnan in north-east of Iran. FT-IR spectra were taken by a Perkin Elmer 65 Model infrared spectrophotometer. XRD patterns were taken by Bruker, D8Advance X-ray diffractometer using $\text{Cu K}\alpha$ radiation. Dibenzothiophene concentration was measured by HPLC (Agilent 1200 model) with column of Zorbax, Eclipse XDB-C₁₈. Capillary gas chromatographs (Agilent technologies 7890 A) and GC-MS (Agilent technologies 5975 C) with 30 m HP-5MS capillary column were used to identify the reaction products. The enjection port temperature was 250 °C and the mass spectra were produced by electron impact (70 eV).

Preparation of photocatalyst

The sol-gel method was used for preparation of TiO_2 nanoparticles. The precursor solution was a mixture containing 5 mL of titanium isopropoxide (TTIP) and 15 mL isopropanol (99%). 250 mL of distilled water was added and the pH of the solution was adjusted by HNO_3 or NH_4OH . The mixture was vigorously stirred until titanium isopropoxide was hydrolyzed and turbid solution was produced. The mixture was heated up to 60-70 °C for 18-20h for peptization. The volume of the solution was then decreased to 50 mL until

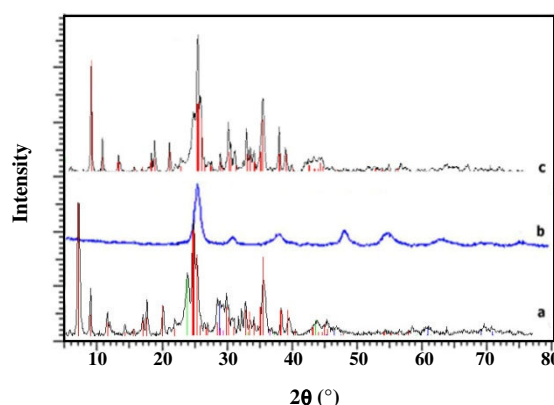


Fig. 1: XRD pattern of TiO_2 /Clinoptilolite (a), TiO_2 (b) and clinoptilolite (c).

a suspension was produced. The solid product was centrifuged, filtered and washed with ethanol and dried at 100 °C. Finally, the prepared TiO_2 was annealed at 200 to 800 °C for 2h [21]. To prepare zeolite-based photocatalyst, 1.0g of the synthesized TiO_2 was mixed with 4.0 g of zeolite by an agate pestle and mortar using ethanol as solvent. The solvent was then removed by evaporation and the photocatalyst was calcinated at 450 °C for 5h [22].

Degradation experiments

To 10 mL of dibenzothiophene solution (100 mg/L in hexane), 0.2 g of photocatalyst were added. The mixture was irradiated by a 30W UV source for known period of time at room temperature. The photocatalyst was then separated by centrifugation and the dibenzothiophene concentration was measured by HPLC. The effect of different parameters on the degradation of dibenzothiophene was studied and optimized.

RESULTS AND DISCUSSIONS

Characterization of the samples

X-ray diffraction patterns of clinoptilolite, TiO_2 and TiO_2 -clinoptilolite are shown in Fig. 1. In the TiO_2 -clinoptilolite pattern, the characteristic diffraction line of TiO_2 at $2\theta=25$ was observed with lower intensity and compared to the clinoptilolite pattern. No major changes in the line intensity and line position were observed. This indicated that TiO_2 was immobilized on the zeolite surface and the zeolite framework remained unchanged during TiO_2 loading [23]. The average particle

size of TiO_2 was determined from the XRD patterns according to the Scherrer's equation:

$$D = K \lambda / \beta \cos \theta \quad (1)$$

Where D is average particle size (nm), λ is wavelength of the radiation, θ is the Bragg's angle and β is the full width at half maximum (radian). The average particle size of TiO_2 was 6.3 nm.

In the FT-IR spectrum of TiO_2 , the absorption peak observed in $3000\text{--}3500\text{ cm}^{-1}$ is assigned to the stretching modes of OH bonds and related to free water molecules. The peak near 558 cm^{-1} is attributed to the stretching vibration of Ti-O bonds. The peak at 1626 cm^{-1} belonged to the adsorbed water (Fig. 2a). The adsorption bands of TiO_2 -clinoptilolite, are mostly similar to those of clinoptilolite (Fig. 2b). The band covers a range from 945 to 950 cm^{-1} corresponding to the stretching vibration of Ti-O-Si and Ti-O-Al. The stretching vibration of O-H (3632 cm^{-1}), corresponding to the surface -OH, becomes weaker after TiO_2 loading, indicating that a certain amount of -OH has been demolished by loading of TiO_2 [24].

The TEM image of the TiO_2 sample is shown in Fig. 3. The average particle size of TiO_2 obtained by this technique was about 6.3 nm and similar to the value calculated by Scherrer's equation.

Fig. 4 shows the SEM image of clinoptilolite (a) and TiO_2 -clinoptilolite (b). Since the pore sizes of clinoptilolite are between $0.4\text{--}0.7\text{ nm}$, the TiO_2 nanoparticles cannot enter into the pores. Therefore, the TiO_2 nanoparticles were loaded on the surface of zeolite. The homogeneous deposition of the TiO_2 on the zeolite surface is obvious from the image [25].

Photodegradation experiments

Effect of irradiation time

To investigate the effect of irradiation time, 10 mL of dibenzothiophene solution (100 mg/L) and 0.2 g photocatalyst were mixed and placed in dark room under UV irradiation for different reaction times. Degradation was increased with the prolonged reaction time up to 6h and then leveled off beyond this time (Fig. 5). As the irradiation time increased more free radicals are produced and enhanced the degradation of dibenzothiophene until the concentration of dibenzothiophene on the photocatalyst surface is reduced.

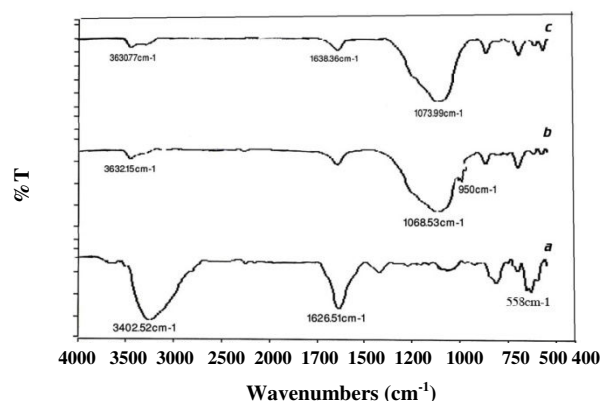


Fig. 2: FTIR spectra of (a) TiO_2 , (b) TiO_2 /Clinoptilolite (20 wt%) and (c) Clinoptilolite.

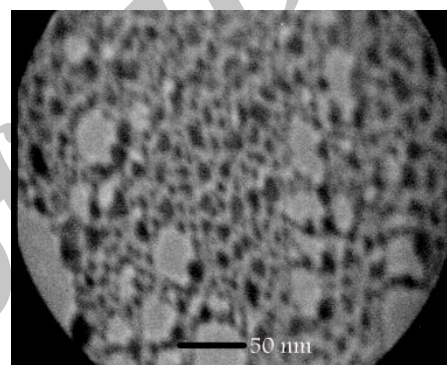


Fig. 3: TEM image of TiO_2 .

Effect of photocatalyst amount

Fig. 6 shows that a swift increase of degradation was occurred as photocatalyst amount was increased. Increasing photocatalyst amount accelerated charge transfer and consequently accelerating photocatalytic oxidation of dibenzothiophene while an excessive amount of photocatalysts would shield the UV light source. Thus, the photocatalyst amount had an optimal value of 0.4 g.

Effect of initial concentration

The effect of initial concentration on degradation of DBT is shown in Fig. 7. The degradation% of DBT decreased with an increase in the initial concentration of DBT. The presumed reason is that when the initial concentration of pollutant is increased, more and more pollutant molecules are adsorbed on the surface of the photocatalyst. The large amount of adsorbed pollutant molecules is thought to have an inhibitive effect on the reaction of pollutant molecules with photogenerated sites

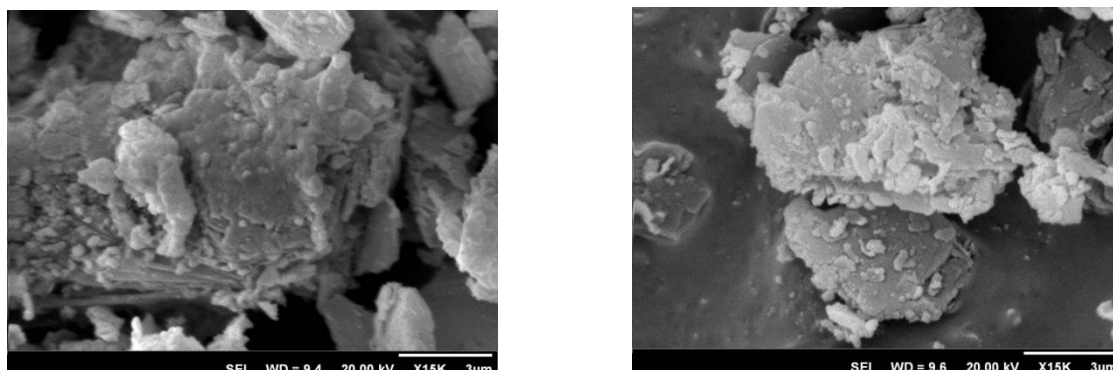


Fig. 4: SEM image of clinoptilolite(a) and TiO₂/Clinoptilolite(b).

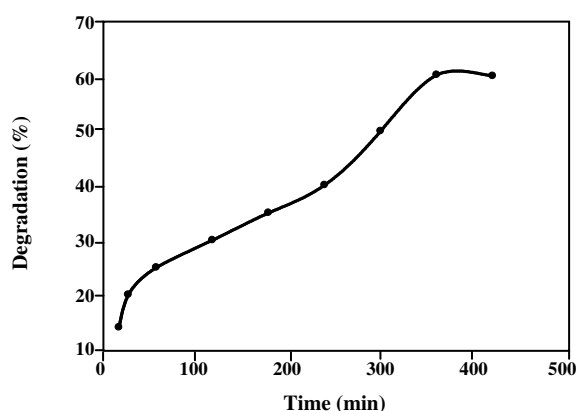


Fig. 5: Effect of irradiation time on degradation of DBT (Initial conc.: 100 mg/L, photocatalyst: 0.2g/L, TiO₂ content: %20).

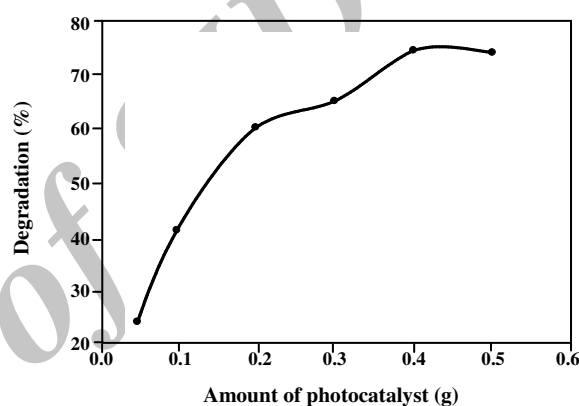


Fig. 6: Effect of the photocatalyst amount on degradation of DBT (Initial conc.: 100 mg/L, irradiation time: 6 h, TiO₂ content: %20).

or hydroxyl radicals, which is due to the lack of sufficient direct contact between them [26]. It was observed that maximal degradation of 70% occurred at concentration of 100 mg/L. Furthermore, it is likely that at higher concentrations the light source intensity is not sufficient for decomposition of dibenzothiophene.

Effect of TiO₂ content

In a series of test, 0.4 g of photocatalyst with different TiO₂ contents (5-20%) were added to 10 mL of dibenzothiophene solution. The samples were placed in dark room under UV irradiation for 5 h. The mixtures were filtered and the amount of dibenzothiophene was measured in their filtrate. It was observed that degradation increased as TiO₂ content of photocatalyst increased up to 15% and then remained constant (Fig. 8). The optimized value was between 15-20% wt of TiO₂. It is assumed that

with increasing of TiO₂ content, first the number of active sites increased and more OH radicals are produced, then agglomeration of TiO₂ particle on the surface of zeolite decreased effective surface area of the photocatalyst.

Kinetics of Reaction

The rate constant for the apparent degradation of DBT was obtained from the pseudo first-order equation:

$$-\ln C_t/C_0 = k_p t \quad (2)$$

Where C_t and C_0 are respectively the concentrations of the compound at time zero and time t (s), and k_p is the first-order rate constant. When $-\ln (C_t/C_0)$ was plotted against t , a straight line was fitted to the data and correlation factor of ($R= 0.973$) was obtained (Fig. 9). This indicated that the reaction followed first order kinetics.

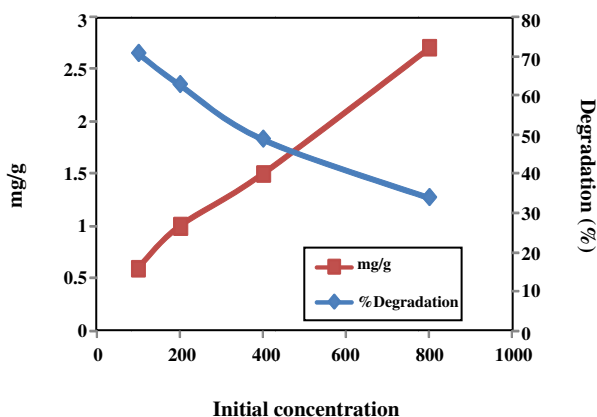


Fig. 7: Effect of initial concentration on degradation of BT (irradiation time: 6 h , TiO_2 content: %20, amount of photocatalyst: 0.4 g/L).

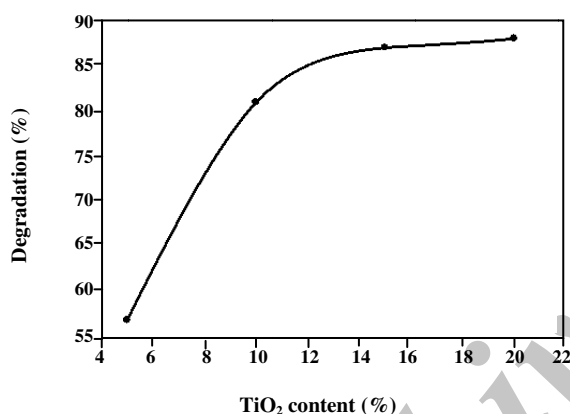


Fig. 8: Effect of TiO_2 content of photocatalyst on degradation of DBT (Irradiation time: 6 h , amount of photocatalyst: 0.4 g/L , initial conc. : 200 mg/L).

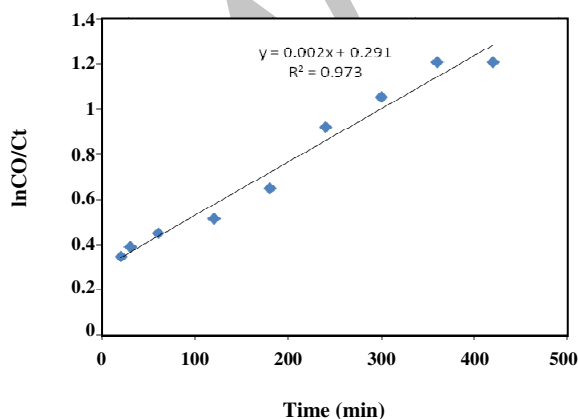


Fig. 9: Pseudo-first-order kinetics for degradation of DBT.

Adsorption of degradation products by β -zeolite

The degradation products were identified by GC-MS techniques. The sulfur containing compounds recognized from ion chromatogram are listed in Table 1.

For deep desulfurization, these compounds are to be removed from the solution. For this purpose, the adsorption method in which β -zeolite was used as adsorbent was applied. To study the removal efficiency, 50 mL of the solution was mixed with 0.3 g of β -zeolite. The mixture was shaken for 24h at room temperature and the solid was separated by centrifugation. The remaining compounds were identified by the ion chromatograms (table 2). The result showed that all sulfur containing compounds including 2-buthyl thiophene, 2-isopentyl thiophene and 2-ethyl thiophene were perfectly adsorbed. Since most of dibenzothiophene was degraded during the photocatalytic reaction, it can be concluded that combination of photodegradation-adsorption processes used in this research is an efficient technique for desulfurization of dibenzothiophene which is a typical aromatic organosulfur compound that cannot be removed by HDS technique.

Reuseability of the photocatalyst

For a catalyst, it is important that the active species are reusable without significant loss of activity. In order to investigate the reusability of the catalyst, desulfurization experiments were performed under similar conditions for four cycles. After each cycle, the photocatalyst was washed with n-hexane solution and calcined at 450 °C for 2h. The desulfurization of dibenzothiophene was performed with the regenerated catalyst under optimized conditions. It was concluded that after 4 cycle 76% of desulfurization efficiency was remained (Fig. 10).

CONCLUSIONS

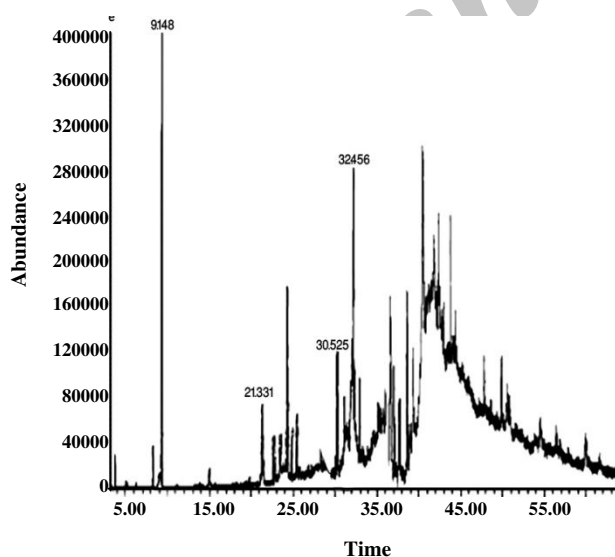
Dibenzothiophene as a typical aromatic organosulfur compound is not efficiently removed by the conventional hydrodesulphurization (HDS) method. In this research a combination of degradation-adsorption technique was used for removal of dibenzothiophene. The results showed that under optimized conditions, the prepared photocatalyst was a desirable candidate for degradation of dibenzothiophene. Furthermore, β -zeolite was able to efficiently adsorb sulfur containing degradation products.

Table 1: The identified degradation products.

Products	Retention Time (min)
Dibenzothiophene	9.34
2-buthyl, thiophene	21.31
2-ethyl, thiophene	30.25
2-isopentyl, thiophen	32.45
3,5-Dimethylisoxazole	36.92
2-furanglycolic acid	8.11
2-furanmethanol	8.27
8-Methoxy-5- carbomethoxychrysene	22.91
1, 5- cyclodecadiene	13.38
4- hydroxyl-2,7,8-trimethoxy-1,4 benzoxazine	37.624
2- pentadecanol	41.14

Table 2: The identified compounds in the solution after adsorption by β -Zeolite.

Products	Retention Time (min)
Dibenzothiophene	9.353
1, 5- cyclodecadiene	13.380
4- hydroxyl-2,7,8-trimethoxy-1,4 benzoxazine	37.624
2- pentadecanol	41.144

**Fig. 10: Ion chromatogram of degraded DBT.**

Therefore, it is suggested that the combined photodegradation-adsorption technique can be used for desulfurization of dibenzothiophene and other aromatic organosulfur compound from organic medium.

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