Combined Oxidative-Adsorptive Method for Elimination of Dibenzothiophene; Degradation by TiO2-CMK-8 Photocatalyst, Adsorption by CMK-8 and SBA-15

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ABSTRACT

In this research, the photocatalytic oxidative method by use of a new photocatalyst prepared based on TiO2 impregnated on the CMK-8 support was employed to degrade dibenzothiophene from organic solution. The degradation products were identified and adsorbed by CMK-8 and SBA-15 adsorbents. The results indicated that at optimized conditions 92% of the pollutant was decomposed. The kinetic of the process was fast and the equilibrium was established within 120 min. 60% degradation was occurred after 25 min. The optimal degradation efficiency was obtained with 0.2 g of the catalyst containing 10 W% of TiO2. The catalyst dose was relatively low compared to the previous reported values. The adsorption experiments indicated that the degradation products, especially the sulfones were mostly removed by the used adsorbents. The catalyst was used for elimination of total sulfur in three real samples of diesel oil containing different concentration of sulfur. The results indicated that the sulfur content was significantly reduced. Regeneration of the used photocatalyst indicated that most of initial activity was retained after catalyst recovery.

Keywords: TiO2-CMK-8 photocatalyst; Dibenzothiophene; Desulfurization; Adsorption; SBA-15

INTRODUCTION

High level of sulfur in transportation fuel is a major source of SOx emission which is responsible for respiratory disorders in humans and poisoning of catalytic converters and many other problems [1]. According to the regulations issued by the United States Environmental Protection Agency, the sulfur content of gasoline and highway diesel fuel must be respectively lowered to 30 and 15 ppmw [2]. The major conventional method for removal of sulfur from crude oil is hydrodesulphurization technique (HDS). In HDS process the sulfur content of the fuel is mostly converted to hydrogen sulfide, but the process requires to high pressures and high temperatures resulting an increased capital and operating costs [3-6]. While the mercaptans, thiophenes, and sulfides are easily removed from oil, but cyclic compounds such as benzothiophene, dibenzothiophene, 4-methyl dibenzothiophene, 4, 6-dimethyl dibenzothiophene due to very high steric hindrance are not properly removed by HDS technique [7]. Therefore, many other methods including oxidative [8], adsorptive [9], biologic and microwave techniques [10] have been considered for removal of sulfur from transportation oil. Oxidative desulfurization (ODS) as one of the most promising method involved the oxidation of sulfur-containing compounds to corresponding sulfones and removal of sulfones by extraction or adsorption method [11,12]. The method does not require expensive catalysts and hydrogen, and proceeds in low temperature and pressure [13]. Moreover, in ODS method the refractory aromatic sulfur compounds such as benzothiophene, dibenzothiophene and their alkyl-substituted derivatives are highly reactive [14,15]. Since sulfur-containing compounds are not degraded themselves under UV/visible irradiations, the ODS technique needs to be proceed with the help of a photocatalyst. TiO2 due to its suitable properties such as high photocatalytic activity, non-toxicity, high thermal and photochemical stability and low cost has been extensively studied [16,17]. Nevertheless, application of TiO2 has some limitations in terms of fast recombination of electron/hole pairs; aggregation of nanoparticles, and being active only in UV and not in sunlight irradiation [18]. Additionally, separation of the used photocatalyst from the solution is always improper and difficult. To overcome these drawbacks and limitations, new photocatalysts with better photocatalytic properties have been prepared by immobilization of TiO2 on the surface of an adequate catalyst support [19]. Many support materials including clays [20], zeolites [21], mesoporous silica [22], and mesoporous carbons [23] have been studied. CMK-8 can be considered as an attractive candidate due to its unique uniform pores, super adsorption capability, special ion-exchange ability, and three-dimensional structure which facilitates the mass transfer kinetics of the adsorption-based applications [24,25].
The purpose of this research was to synthesis CMK-8, and uses it as catalyst support for TiO$_2$, and to use the synthesized photocatalyst for degradation of dibenzothiophene.

**MATERIALS AND METHODS**

The chemicals; dibenzothiophene (DBT), titanium isopropoxide, Pluronic P123, HCl, H$_2$SO$_4$, i-propyl alcohol, tetraethyl-orthosilicate (TEOS) n-hexane and hydrogen peroxide (30%) were purchased from Merck Company.

FT-IR spectra were taken by a Perkin Elmer 65 Model infrared spectrophotometer. XRD patterns were obtained by Bruker, D8Advance X-ray diffractometer using Cu K$_{\alpha}$ as radiation source. The BET surface areas were determined by BEL SORP 18 series instrument. Dibenzothiophene concentration was measured by HPLC (Agilent 1200 model) with a Zorbax, Eclipse XDB-C18 column. The photodegradation products were identified by a capillary gas chromatographs (Agilent technologies 7890 A) and GC-MS (Agilent technologies 5975 C) with 30 m HP-5MS capillary column. The ejection port temperature was 250°C and the mass spectra were produced by electron impact (70 ev). The UV-visible diffuse reflection spectra were recorded using a Cary 100 spectrophotometer in the range 200 to 800 nm.

**Synthesis of CMK-8**

The synthesis of CMK-8 was prepared based on KIT-6 structure which was synthesized according to the modified procedure described by Kim [26] . Briefly, known amount of Pluronic P123 (poly (ethylene oxide)-poly (propylene oxide) - poly (ethylene oxide), EO20-PPO$_{70}$-PEO$_{20}$ was dissolved in HCl solution, diluted with deionized water, and shaken until proper dissolution. A few mL of butanol was added and the mixture was stirred until a homogenous solution was obtained. The suspension was heated at 100°C for 8 h; the solid was separated, dried at 100°C and calcined at 550°C for 6 h.  

To prepare CMK-8, 1.0 g of as-synthesized KIT-6 was added to a mixture containing known amount of sucrose dissolved in deionized water acidified with H$_2$SO$_4$. The mixture was shaken for 60 min; the solid was separated, dried at 100°C and then calcined at 160°C for 6 h. The carbon silica composite was pyrolyzed in nitrogen atmosphere at 900°C for 4 h and the carbon mesoporous was recovered by dissolving the silica template in ethanolic sodium hydroxide (50% water 50% ethanol v/v). Finally the product was filtered and washed with ethanol and dried at 100°C for 12 h [27].

**Preparation of TiO$_2$/CMK-8**

TiO$_2$/CMK-8 (2 wt% TiO$_2$) was prepared by adding 5.95 mL of i-propyl alcohol and 0.074 mL titanium (IV) isopropoxide to 1.0 g of CMK-8. The mixture was heated at 100°C until the TiO$_2$ particles were gradually formed within the CMK-8 structure. The composite was calcined at 700°C in N$_2$ atmosphere. In the same manner, TiO$_2$/CMK-8 with different TiO$_2$ content (5%, 10% and 20%) was prepared by variation the amount of titanium (IV) isopropoxide [28].

**Initial photodegradation tests**

A mixture containing 0.2 g of TiO$_2$/CMK-8 and 10 mL of dibenzothiophene (100 mg.L$^{-1}$ in hexane) was irradiated under a 30W UV source for known period. The photocatalyst was separated by centrifugation and the dibenzothiophene concentration was measured in the remaining solution. The UV-Vis spectrum of the solution before and after irradiation was taken (Figure 1S). The spectrum showed that the intensity of the peak at 242 nm belonged to dibenzothiophene was abruptly decreased indicating that the pollutant was effectively degraded under employed experimental conditions. The measurement was also performed by HPLC technique. The recorded chromatogram showed that the peak of dibenzothiophene at retention time of 3.56 was almost disappeared after irradiation (Figure 2S). To obtain the highest degradation rate, the experimental conditions such as pollutant concentration, catalyst dose, TiO$_2$ content, temperature were optimized. The influence of some oxidants on the degradation process was also examined.
RESULTS AND DISCUSSION

Characterization of the photocatalyst

In the FT-IR spectrum of TiO₂, the absorption band appeared at 3402 cm⁻¹ was assigned to the stretching modes of OH bonds related to water molecules adsorbed on the surface of the compound. The strong absorption band at 580 cm⁻¹ was attributed to the stretching vibration of Ti-O bonds and the peak at 1600 cm⁻¹ belonged to the adsorbed water molecules (Figure 1a).

In the FTIR spectra of CMK-8 and TiO₂/CMK-8 (Figure 1b and 1c), the adsorption band observed around 3423 and 3302 cm⁻¹ belonged respectively to the O-H stretching vibration of the adsorbed water molecules. In the spectrum of CMK-8, the broad band appeared at 1128 cm⁻¹ was attributed to the stretching vibration of the C-O bonds. This peak was shifted to 1100 cm⁻¹ when CMK-8 was combined with TiO₂. The C-O stretching vibrations of carbonyl and/or carboxyl groups were found around 1620 cm⁻¹ in CMK-8 and at 1615 in TiO₂/CMK-8 sample [29]. The characteristic peak of TiO₂ which was appeared at 580 cm⁻¹ in the bulk TiO₂ was shifted to 628 cm⁻¹ when TiO₂ was immobilized into the CMK-8 structure.

The ordered arrangement of carbon nano rods in CMK-8 gives rise to the well-resolved XRD diffraction lines [29]. In the low-angle XRD pattern of CMK-8 illustrated in (Figure 2a), the characteristic strong peak at 1.16° indexed as (211) of 3D cubic Ia3d symmetry of CMK-8 was observed.
In the XRD pattern of TiO$_2$ (Figure 2b), the diffraction lines at 2θ = 25.3°, 37.8°, 46.0°, 55°, 62.1°, 70° and 75° assigned to the diffractions of (101), (004), (200), (105), (204), (116) and (215) crystal planes of the anatase phase were observed. The lines position and intensity agreed well with the standard pattern of anatase [JCPDS No. 21-1272] [30].

In the TiO$_2$/CMK-8 pattern (Figure 2c), the characteristic diffraction lines of TiO$_2$ were clearly observed. The position and the relative intensity of the lines remained intact indicating that impregnation of TiO$_2$ to the CMK-8 structure did not change the framework structure of TiO$_2$ suggesting that TiO$_2$ preserve its photocatalytic activity in the newly synthesized photocatalyst [23]. The particle size of TiO$_2$ was determined from the XRD patterns according to the Scherer's equation:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Where $D$ is average particle size (nm), $\lambda$ is wavelength of the radiation, $\theta$ is the Bragg’s angle and $\beta$ is the full width at half maximum (radian). The average particle size of TiO$_2$ was 12 nm and close to the value obtained from TEM image (Figure 3).

![Figure 3: TEM images of CMK-8 (a), TiO$_2$/CMK-8 (b).](image)

The BET specific surface areas of the samples were determined by BEL SORP 18 series instrument. Three dimensional ordered mesoporous carbons (CMK-8) are characterized by high surface area (>1000 m$^2$/g), large pore volumes, and a highly regular interconnected pore structure that could allow for a good dispersion of catalyst nanoparticles [29]. The synthesized CMK-8 of this work showed surface area of 1043 m$^2$/g and pore diameters of 3.06 nm. After incorporation of TiO$_2$, the surface area of composite was reduced to 433 m$^2$/g, TiO$_2$ molecules grafted in the pores of the host structure lowered the pore volume of the composite but the opening of the pore was sufficiently wide (Table 1). These observations confirmed that TiO$_2$/CMK-8 photocatalyst had the capability of a desirable photocatalyst due to its reasonable surface area and homogenous distribution of nano-sized TiO$_2$ particles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMK-8</td>
<td>1043</td>
<td>0.79</td>
<td>3.06</td>
</tr>
<tr>
<td>TiO$_2$/CMK-8</td>
<td>433.2</td>
<td>0.61</td>
<td>3.14</td>
</tr>
</tbody>
</table>

The TEM image of CMK-8/TiO$_2$ (10%) displayed in Figure 3b, showed that dark spots images corresponding to TiO$_2$ nanoparticles are incorporated inside the structure of CMK-8, in some parts of the image, the TiO$_2$ nanoparticles are aggregated on the external surface of CMK-8. Although the TiO$_2$ particles are placed inside the CMK-8 pore at the beginning of synthesis but TiO$_2$ phase was segregated onto the external surface of CMK-8 during the heating process at 700 °C [28]. This enhanced the photocatalytic performance of the composite by generation of e/h pairs on the surface of the composite where the pollutant molecules are adsorbed.

**Optimizing of degradation efficiency**

Photocatalytic activity of TiO$_2$-based photocatalysts can be influenced by various parameters such as surface area, particle size and pH of the solution, catalyst dose and TiO$_2$ content. To obtain the highest possible degradation efficiency the parameters were optimized as follows:

**Optimizing of TiO$_2$ content**

TiO$_2$ content of the photocatalyst played an important role in the photodegradation reaction. By increasing of TiO$_2$
content, the efficiency of the photocatalyst was increased. The trend continued until the TiO$_2$ content was 10% and then the degradation efficiency was lowered (Figure 4). The decrease observed beyond of 10% of TiO$_2$ was attributed to the aggregation of photocatalyst particles resulting lowered surface area and lower adsorption of pollutant molecules. The optimized catalyst loading of the synthesized catalyst of this work was comparable with the values reported for similar experiments. Park et al. used TiO$_2$ impregnated on mesoporous carbon for degradation of rhodamine and reported that the maximal degradation was occurred with TiO$_2$ loading of 10% [28]. Yaun et al. used mesoporous phosphotungstic acid/TiO$_2$ nanocomposite for photodegradation of dibenzothiophene and reported that 95% degradation was occurred at TiO$_2$ content of 20% [31].

![Figure 4: Effect of TiO$_2$ content on degradation of DBT (Irradiation time: 240 min, photocatalyst dose: 0.2 g, initial concentration: 400 mg/L).](image)

**Minimizing the catalyst dose**

It is advantageous to obtain higher degradation efficiency with lower dose of a photocatalyst. In order to optimize the catalyst dose, the degradation experiments were carried out with various catalyst dose of TiO$_2$/CMK-8 (10 wt. %) in the range of 0.05 to 0.50 g (Figure 5). By increasing the photocatalyst dose the charge transfer to the pollutant molecules was accelerated and consequently photocatalytic oxidation of dibenzothiophene was enhanced. The excessive amount of photocatalysts suppressed the degradation process by scattering of the incident UV photons and by aggregation of the photocatalyst particles leading to lower surface area of the catalyst. Therefore, beyond the catalyst loading of 0.2 g the efficiency of the photocatalyst was significantly decreased [32]. Faghihian et al. who studied the removal of dibenzothiophene by use of TiO$_2$ impregnated into zeolite clinoptilolite reported that for degradation of 100 mg.L$^{-1}$ dibenzothiophene solution, the optimized catalyst dose was 0.4 g [24]. Arnalo et al. used CuO/GC photocatalyst for degradation of dibenzothiophene from diesel oil and concluded that proper degradation was occurred with catalyst loading of 0.3 g. [33].

![Figure 5: Effect of catalyst dose on degradation of DBT (irradiation time: 220 min, Initial conc: 400 mg/L, TiO$_2$ content: 10%).](image)
Optimizing the contact time

The effect of reaction time on the conversion of DBT was evaluated from 10 to 240 min (Figure 6). At the beginning, the conversion was very fast and about 60% of degradation was occurred within 25 min. Then the process forwarded more gradual until the equilibration was established within 120 min with maximal degradation of 92%. By increasing irradiation time more OH radicals were produced and the conversion was enhanced until the concentration of dibenzothiophene on the photocatalyst surface was reduced [24]. The kinetic of degradation process of this work was faster than the previous reported values. Lio et al. used phosphotangestic acid impregnated on functionalized MCM-41 for photocatalytic degradation of dibenzothiophene and reported that optimized degradation was obtained within 150 min [34]. Zhao et al. used modified molecular sieve photocatalyst, M₂(PCAN)₂-W-HZSM-5 for degradation of dibenzothiophene and reported that the optimized reaction time was 180 min [35].

![Figure 6: Effect of irradiation time on degradation of DBT (irradiation time: 220 min, photocatalyst: 0.2g, TiO₂ content: 10%).](image)

The constant rate for the decomposition of DBT was calculated from the first-order kinetic model as follows:

\[-\frac{dc}{dt} = Ke\]  \hspace{1cm} (2)

Integral on both sides of Equation (2) give:

\[-\int_0^\infty \frac{dc}{C} = \ln \frac{c_t}{c_0} = Kt\]  \hspace{1cm} (3)

\[c_t = c_0 e^{kt}\]  \hspace{1cm} (4)

By plotting of ln(C₀/Cₜ) versus t, a straight line with slope k was obtained (Figure 7). The rate constant K was 0.0197 min⁻¹. The R² value indicated that the reaction kinetics was well fitted the first-order kinetic model.

![Figure 7: Kinetics study, Plot of lnC₀Cₜ versus time.](image)
Effectiveness of photocatalyst for different concentration of DBT

Since different crude oils and their derivate products contain various concentration of dibenzothiophene, the capability of the synthesized photocatalyst for degradation of varying concentration of dibenzothiophene was evaluated within the concentration range of 100-800 mg.L⁻¹ (Figure 6).

Under optimized conditions, for 400 mg.g⁻¹ solution, the maximal degradation efficiency of 80% was obtained. However, at concentration of 800 mg.g⁻¹, degradation efficiency of 78% was obtained. It is presumed that when the initial concentration of pollutant increased, more pollutant molecules were adsorbed on the surface of the photocatalyst leading to higher interactions between the pollutant molecules and photogenerated radicals. When the adsorption is beyond a certain amount, the direct contact between the molecules and the photogenerated radicals was limited and the degradation efficiency was lowered [36]. Furthermore, it is likely that at higher concentrations of DBT the penetration of light photons in to the depth of the solution was limited and consequently the generated radicals were insufficient for decomposition of the pollutant molecules [37]. However, at concentration of 800 mg.g⁻¹, the degradation efficiency of 78% was obtained. From the results of this experiment it was concluded that the performance of the photocatalyst of this work to degrade the higher concentration of dibenzothiophene is better that the previous reported values. Haung et al. used TiO₂ photocatalyst impregnated in mesoporous material for oxidative degradation of dibenzothiophene and concluded that with 0.1 g of photocatalyst the optimized degradation was obtained for 300 mg.L⁻¹ solution [38]. Moradi used La/PEG modified with TiO₂ for decomposition of dibenzothiophene and reported that maximal degradation was obtained for 250 mg.L⁻¹ solution [39].

Effect of hydrogen peroxide on the degradation efficiency

The previous studies has been shown that addition of strong oxidant reagents such as H₂O₂ had significant impact on the degradation process [24]. The presence of H₂O₂ at low concentration enhanced the degradation efficiency through production of hydroxyl radical OH⁻ by photo dissociation of H₂O₂ (equation 5) while at higher concentration hydrogen peroxide acting as electron scavenger and suppresses the degradation efficiency (equation 6 and 7) [32]. The experiments performed in this work indicated that addition of hydrogen peroxide accelerated the photocatalytic degradation of DBT and the maximal impact was observed by addition 1.5 mL of H₂O₂ (Figure 8).

![Figure 8: Effect of the oxidant amount on degradation of DBT (irradiation time: 220 min, Initial conc: 400 mg/L, photocatalyst: 0.2g, TiO₂ content: 10%).](image)

\[
\text{H}_2\text{O}_2 + e^- \rightarrow \text{OH}^- + \text{OH}^-
\]

Further increasing of hydrogen peroxide decreased the degradation efficiency through adsorption of hydroxyl radical [38].

\[
\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{OH}_2^-
\]

\[
\text{OH}_2^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}_2
\]

Identification and adsorption of degradation products

The degradation products were identified by GC-MS technique. Several products including isooctane, cyclohexanone, decane, biphenyl, octadecane, dibenzothiophene sulfone and isoindole were detected as degradation products. The intensity of the peak appeared at 35.30 belong to dibenzothiophene sulfone and the peak observed at retention time
27.79 belonged to the remaining dibenzothiophene was high (Table 2 and Figure 9). For removal of the degradation products, two adsorbents SBA-15 and CMK-8 were employed. After separation of the used photocatalyst, into 25 mL of the remaining solution 0.4 g of the adsorbent was added and the mixture was shaken for 6 h at room temperature. After equilibration, the adsorbent was separated and the remaining compounds were identified by GC-MS technique. The encouraging results given in Figure 9, and Table 3 and 4, indicated that by using CMK-8 adsorbent, the degradation products especially dibenzothiophene sulfone was properly removed. Additionally the intensity of the peak related to the remaining dibenzothiophene was significantly decreased. Application of SBA-15 also decreased the concentration of the degradation products especially dibenzothiophene sulfone, but this adsorbent had lower efficiency for removal of the remaining dibenzothiophene. The concentration of isooctane after adsorption processes remained high indicating that the affinity of the employed adsorbents towards this product was insufficient. But the presence of this compound is not harmful for the fuels.

Table 2: Identified degradation products before adsorption.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Retention time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isooctane</td>
<td>3.45</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>5.63</td>
</tr>
<tr>
<td>Decane</td>
<td>7.56</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>18.69</td>
</tr>
<tr>
<td>Octadecane</td>
<td>23.28</td>
</tr>
<tr>
<td>Dibenzothiophene</td>
<td>27.79</td>
</tr>
<tr>
<td>Dibenzothiophene sulfone</td>
<td>35.3</td>
</tr>
<tr>
<td>Isoindole</td>
<td>40.27</td>
</tr>
<tr>
<td>Benzene dicarboxylic acid</td>
<td>41.08</td>
</tr>
</tbody>
</table>

Figure 9: The chromatograms of degradation products; before adsorption (a), after adsorption by SBA-15 (b), and after adsorption by CMK-8 (c).
Table 3: Remaining degradation products after adsorption by SBA-15.

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Retention time (time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isooctane</td>
<td>3.48</td>
</tr>
<tr>
<td>Decane</td>
<td>7.56</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>18.69</td>
</tr>
<tr>
<td>Dibenzothiophene</td>
<td>27.78</td>
</tr>
<tr>
<td>Dibenzothiophene sulfone</td>
<td>35.24</td>
</tr>
<tr>
<td>Benzene dicarboxylic acid</td>
<td>41.07</td>
</tr>
</tbody>
</table>

Table 4: Remaining degradation products after adsorption by CMK-8.

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isooctane</td>
<td>3.48</td>
</tr>
<tr>
<td>Decane</td>
<td>7.56</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>18.69</td>
</tr>
<tr>
<td>Dibenzothiophene</td>
<td>27.78</td>
</tr>
<tr>
<td>Dibenzothiophene sulfone</td>
<td>35.24</td>
</tr>
<tr>
<td>Benzene dicarboxylic acid</td>
<td>41.07</td>
</tr>
</tbody>
</table>

Regeneration of the used photocatalyst

The reusability and stability of the photocatalyst are important for industrial applications. To investigate the regeneration of the TiO$_2$/CMK-8 (10 wt%), the used photocatalyst was separated from degradation solution, washed with n-hexane, and heated at 400 °C for 60 min. The regenerated catalyst was re-used for photodegradation process under optimized conditions. The regeneration-reapplication was repeated for four consecutive cycles (Figure 10). The results indicated that most of initial activity of the photocatalyst (TiO$_2$/CMK-8 (10 wt %) was retained after regeneration.

Application of the combined oxidative-adsorptive methods for real samples

To study the capability of the suggested method for lowering the total sulfur content of the real samples, the experiments was conducted on three diesel oil samples containing 230, 1440 and 6250 mg.L$^{-1}$ total sulfur. To 50 mL of the sample 1.5 g of the synthesized photocatalyst and 1.5 mL of hydrogen peroxide were added. The mixture was homogenized and illuminated under UV source for 120 min. The mixture was centrifuged, the catalyst was removed. To the remaining solution 0.5 g of the adsorbents (SBA-15 or CMK-8) was added. The mixture was shaken for 8 h and the adsorbent was separated by centrifugation. The total sulfur content was measured in the supernatant solution. The experiments indicated that the combined oxidative-adsorptive method used in this work had the capability to reduce the total sulfur content of the diesel oil as shown in Table 5. The elimination of higher 50% was very interesting especially in high sulfur samples.
Table 5: Elimination of total sulfur in three different diesel oils.

<table>
<thead>
<tr>
<th>No.</th>
<th>Total sulfur $\text{mg.L}^{-1}$</th>
<th>SBA-15 $\text{mg.L}^{-1}$</th>
<th>Reduction (%)</th>
<th>CMK-8 $\text{mg.L}^{-1}$</th>
<th>Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6000</td>
<td>3000</td>
<td>50</td>
<td>2800</td>
<td>53.3</td>
</tr>
<tr>
<td>2</td>
<td>1440</td>
<td>680</td>
<td>52.7</td>
<td>650</td>
<td>54.8</td>
</tr>
<tr>
<td>3</td>
<td>230</td>
<td>110</td>
<td>52.1</td>
<td>96</td>
<td>58.2</td>
</tr>
</tbody>
</table>

CONCLUSION

By employment of the new heterogeneous photocatalyst prepared by impregnation of TiO$_2$ on the CMK-8 structure, the photodegradation of dibenzothiophene dissolved in organic solution was studied. High degradation efficiency was obtained even with the solution in which the concentration of the pollutant was 800 mg L$^{-1}$. The degradation products were identified and it was concluded that dibenzothiophene sulfone was one of the main products. Elimination of the degradation products and the remaining dibenzothiophene was examined by use of CMK-8 and SBA-15 adsorbents. The experiments indicated that the degradation products, especially the sulfons were mostly removed by the used adsorbents. Application of the method for elimination of the total sulfur of diesel oil samples showed that the method had high performance for reducing of the total sulfur content of the diesel oils. Upon regeneration, the used photocatalyst retained most of its initial activity.

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