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Photocatalytic degradation of phenolic compound (phenol, resorcinol and cresol) by titanium dioxide photocatalyst on ordered mesoporous carbon (CMK-3) support under UV irradiation

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ABSTRACT

The photocatalytic degradation of phenolic compounds (phenol, *m*-cresol and resorcinol) was investigated by the TiO_2 nanoparticles on ordered mesoporous carbon (CMK-3) support, as a nanocatalyst. CMK-3 and TiO_2/CMK-3 were synthesized using SBA-15 as a hard template and their properties were determined by transmission electron microscopy, X-ray powder diffraction and N_2 adsorption–desorption. The results showed that CMK-3 was well synthesized and TiO_2 was properly incorporated into CMK-3. The effect of different parameters such as pH, catalyst concentration, phenolic compound concentration and irradiation time on TiO_2/CMK-3 catalytic activity was investigated. The results showed that photocatalytic degradation of phenolic compounds was strongly influenced by these factors and the optimum conditions for removing the contaminants were pH = 6, TiO_2/CMK-3 concentration of 0.15 g/L, phenolic compound concentration of 100 mg/L and irradiation time of 150 min. Under optimum conditions, the total organic carbon removal efficiency for phenol, *m*-cresol and resorcinol was observed to be 74%, 62%, and 78%, respectively. The highest photo-degradation efficiency was obtained at the slightly acidic and near to neutral pH values compared with the alkaline and acidic range. The stability and reusability of TiO_2/CMK-3 nanocatalyst were observed to be more than five times which it reveals that the TiO_2/CMK-3 can be considered as a promising catalyst for the long-term degradation of phenolic compounds from aqueous solutions.

Keywords: Photocatalytic degradation; UV irradiation; Phenolic compounds; TiO_2/CMK-3; CMK-3

1. Introduction

Phenol and its compounds are broadly used in textile, paper, pesticides and petrochemical industries, which have recently been a threat to aquatic environments due to low biodegradability [1]. These compounds are classified as priority pollutants due to their chronic toxicity, the nature of biological stability and increasing the toxicological intermediates after biological degradation in the viewpoint of regulatory agencies [2,3]. Phenol and its derivatives are found in concentrations of more than 1 mg/L in industrial wastewater and in the range of 0.01×10^{-3} to 2×10^{-3} mg/L in surface water [4]. Discharging these materials from industrial wastewater to the environment, in the long-term, causes health problems such as skin irritation, damage to the central nervous system and the digestive tract [5,6]. Therefore, the degradation of phenol and its compounds in wastewater prior to release into the environment is essential and important.

In recent years, various technologies have been proposed for the removal of phenolic compounds such as adsorption, membrane process, biological purification and chemical coagulation [7,8]. However, these common

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technologies are not able to provide complete degradation of phenolic compounds and, even, they generate secondary pollution with high concentrations [8]. Compared with these technologies, the advanced oxidation processes (AOPs) using hydroxyl radical with $E = 2.8$ V are able to degrade the organic pollutants completely and to convert them into minerals, CO_2 and H_2O. Among the AOPs, the heterogeneous photocatalytic, as a green technology, has attracted various studies on the degradation of atmospheric and organic compounds. In this process, the organic pollutants are destroyed in the presence of light source, semiconductor photocatalyst and oxidizing agent such as air or oxygen [9]. In the photocatalytic process, various photocatalytic agents such as SnO_2, SiO_2, ZnO_2, WO_3, Fe_2O_3 and TiO_2 have been used to accelerate the photo-degradation and degradation of organic compounds [10]. Meanwhile, TiO_2-based photo-degradation has recently attracted many studies due to its benefits including the complete removal of organic pollutants, low-cost, chemical stability and non-toxicity [11]. In the TiO_2 photocatalytic process, the pollutants are degraded through h^+, hydroxyl radical ($OH^\bullet$) and superoxide radical anions generated ($O_2^{\bullet-}$) [12]. In this process, the brightness of the TiO_2 surface with sufficient energy produces a positive hole (h^+) in the valence band and electron (e) in the conduction band Eq. (1). Positive hole, in addition to the direct degradation of pollutant Eqs. (3) and (4), causes the OH^- formation through the penetration into the TiO_2 surface and reaction with absorbed water molecules Eq. (2). At the same time, the electron in the conduction band, by decreasing the oxygen absorbed on the TiO_2 surface, causes the formation of $O_2^{\bullet-}$ Eq. (5) and, as a result, leads to the degradation of the pollutant [13,14].

$$TiO_2 + h_v \rightarrow e^- + h^+ \tag{1}$$

$$h^+ + \text{Pollutant} \rightarrow CO_2 \tag{2}$$

$$h^+ + H_2O \rightarrow OH^\bullet + H^+ \tag{3}$$

$$OH^\bullet + \text{Pollutant} \rightarrow H_2O + CO_2 \tag{4}$$

$$e^- + O_2 \rightarrow O_2^{\bullet-} \tag{5}$$

One of the benefits of heterogeneous photocatalytic systems compared with homogenous systems is the easier collection of photocatalysts in the heterogeneous system after the reactions. Therefore, it is important to use a suitable substrate as photocatalyst. In this regard, various types of support for TiO_2 such as perlite [14], zeolite [15], clinoptilolite [16], multiwalled carbon nanotubes [17], activated carbon [18] and clay [19] have been studied. Among these materials, activated carbon has been utilized by many studies as support in photocatalytic processes because of its excellent surface area, well-developed pore structure and high adsorption capacity [20,21]. Although these catalysts do not have photocatalytic activity, they significantly improve the photocatalytic reaction between the pollutant and the TiO_2 by increasing the adsorption of pollutants on the surface [20]. In most of the previous studies, the photocatalytic process based on TiO_2/AC composite has been successfully used to treat various pollutants such as phenol [22], diclofenac, paracetamol [20] and toluene [23]. However, a significant decrease in the performance of this process has been reported based on the adsorption efficiency of TiO_2 particles on AC and mechanical mixing of TiO_2 anatase and AC powder. In addition, the irregular structure of AC leads to problems for the structural property of TiO_2 on AC composite [24]. In addition, the use of AC in the adsorption of bulky adsorbates is limited due to the microporous dimensions [25]. To overcome these disadvantages, the use of ordered mesoporous carbons has been considered due to its high surface areas, large and tunable pore sizes, and large pore volumes, providing the suitable bed for the catalyst [24,25]. These carbonaceous materials are commonly obtained by the carbonization of the natural and artificial precursor and activation of them [26]. Recently, the unique properties of mesoporous carbon have increased its application in various fields such as support catalyst and supercapacitors [27]. In addition to the open pore structure and mesoporous properties, the high efficiency of these materials is reported in the removal of some organic compounds through the adsorption process [25]. An ordered mesoporous carbon with a hexagonal two-dimensional structure is synthesized by carbonizing the silica mesoporous materials such as uniform pore size SBA-15 [24,28]. This material, in comparison with other ordered mesoporous carbons, has found more attention due to its unique properties such as high surface area, large pore volume, excellent synthesis and excellent physical and chemical stability in environmental fields, electrochemical, energy storage [29]. Recently, the adsorption of pollutants and improvement of oxidation processes by the CMK-3 has been reported. Ezzeddine et al. [31] studied the adsorption of methylene blue on CMK-3 and found that CMK-3 had an extremely high adsorption capacity [30]. Tanthapanichakoon et al. [31] reported that mesoporous carbon adsorption capacity is much higher than the activated carbon. Hu et al. [32] investigated the phenol oxidation by Fe/CMK-3 and found that Fe/CMK-3, in addition to adsorbing and oxidizing the phenol, has the ability to easily separate from the solution with minimal leaching [32].

The aim of this study is to investigate the photocatalytic degradation of the phenolic compound (phenol, resorcinol and cresol) by titanium dioxide photocatalyst on ordered mesoporous carbon (CMK-3) support under UV irradiation. In this study, TiO_2/CMK-3 was synthesized using ordered mesoporous carbon as the support and titanium isopropoxide as the titanium source. The effect of different parameters such as pH, catalyst concentration, phenolic compound concentration and irradiation time was studied. The stability and reusability of TiO_2/CMK-3 catalyst were investigated in even continuous cycles under optimum conditions. Finally, the efficiency of photocatalytic process in the removal of total organic carbon (TOC) was evaluated in optimum operating conditions.

2. Materials

All chemicals used in this study were of analytical grade. Tetraethyl orthosilicate (TEOS, 98%) as a silica source, titanium (IV) isopropoxide (TIP 97%) as a titanium source and pluronic P123 (EO20PO70EO20) as a surfactant were purchased from Sigma-Aldrich CO., USA. The sucrose, as a carbon source, sodium hydroxide (NaOH), ethanol, sulfuric acid (H_2SO_4, 98%) and isopropyl alcohol were provided by Merck CO., Germany. Deionized double-distilled water was utilized for all of the experiments.

2.1. Preparation of SBA-15, CMK-3 and TiO_2/CMK-3

2.1.1. Preparation of SBA-15

In order to synthesize the CMK-3, the SBA-15 was applied as the template. SBA-15 was synthesized as described by Zhao et al. [33].

The typical synthesis process was performed as follows: 2 g P123 was dissolved in 60 mL of 2 M HCl solution and, after that, 15 mL deionized water at 40°C and 4.25 g of TEOS were added. After magnetically stirring the solution at 40°C for 24 h, the mixture was placed in the autoclave at 100°C for 48 h. The resultant was recovered by filtration with 0.45 μm Whatman filter and was initially rinsed several times with distilled water and ethanol (25%) and was then washed by distilled water. Afterward, the filtrated solids were calcined at 550°C in the air at a ramping rate of 1°C/min and it was kept at this temperature for 12 h to eliminate the organic template of P123.

2.1.2. Preparation of CMK-3

CMK-3 was prepared according to Jun et al. [34]. SBA-15 was used as a hard template. Initially, 1 g SBA-15 was added to a solution obtained by dissolving 1.25 g sucrose and 0.14 g H_2SO_4 (98%) in 5 mL H_2O. The resulting mixture was located in the oven at 100°C for 6 h. The oven temperature was later increased to 160°C for 6 h. In order to obtain the polymerized and carbonized sucrose inside the pores of the silica template, 0.8 g of sucrose, 0.09 g of H_2SO_4 and 5 mL of water were again added to the pretreated sample and the mixture was then subjected to thermal treatment as described earlier. The composite was then pyrolyzed in a nitrogen flow (purity = 99.999% and flow rate = 30–50 mL min^{-1}) at 900°C and was kept under these conditions for 6 h for carbonization of the polymer. The mesoporous carbon (CMK-3) was obtained by eliminating the silica template using a 1 M aqueous ethanolic NaOH solution (50 vol.% NaOH solution and 50 vol.% ethanol) twice at room temperature followed by filtration, washing and drying at 120°C for 4 h.

2.1.3. Preparation of TiO_2/CMK-3

TiO_2/CMK-3 with 5 wt.% of TiO_2 was prepared by adding a solution of 5.95 mL isopropyl alcohol and 0.19 mL titanium(IV) isopropoxide (TIP, 97%, Sigma-Aldrich) into 1.0 g of CMK-3, and then TiO_2 particles were generated by placing in an oven at 100°C with water vapor for 6 h. The final calcination was performed at 700°C for 2 h in the argon atmosphere [24].

2.2. Characterization methods

XRD patterns of the resultant material were collected using a Philips PW 1730 X-ray diffractometer, The Netherlands. The diffractograms were recorded in the 2θ range of 0.5°–5° with a 2θ step size of 0.05°. The specific surface area of the TiO_2/CMK-3 was calculated according to Brunauer–Emmett–Teller method, and pore size distribution curves were obtained from the analysis of nitrogen adsorption isotherms using Barrett–Joyner–Halenda method on a BELSORP-mini II at –196°C (77 K). Before each measurement, the sample was heated under vacuum at 450°C. Transmission electron microscopy (TEM) images for the determination of TiO_2/CMK-3 dispersion and morphology of samples were obtained using a Zeiss EM900, Germany.

2.3. Photo-degradation experiments

In this study, the photocatalytic activity of TiO_2/CMK-3 photocatalyst in degradation of the phenolic compound (phenol, *m*-cresol and resorcinol) was assessed in a photocatalytic reactor under UV light irradiation at room temperature. The light source was the medium pressure UV lamp (150 W). The initial pH was adjusted by the addition of 0.1 N HCl and/or 0.1 N NaOH. The desired conditions for initial pH (4, 5, 6, 7, 8, 9, and 10), TiO_2/CMK-3 concentration (0.05, 0.1, 0.15, 0.3, and 0.5 g/L), reaction time (30, 60, 90, 120, and 150 min) and phenolic compound concentration (50, 100, 150, and 200 mg/L) were consecutively studied. In each experiment, certain concentration of photocatalyst was added into 250 mL of phenolic solutions under magnetic stirring (150 rpm at 25°C) without UV light until reaching the equilibrium (typically 1 h), and then the suspension was irradiated under UV light. After that, approximately 5 mL of the suspension sample was withdrawn at the predetermined time interval and separated by centrifuge at 4,000 rpm for 5 min and then filtered through a 0.45 μm syringe filter to achieve a clear supernatant for analysis of the concentrations of the solutes. The concentration of phenol, *m*-cresol and resorcinol in the supernatant was analyzed using a UV/Vis spectrophotometer (6305 UV/Vis Jenway spectrophotometer, UK) with the wavelength at 270, 272, and 313 nm, respectively. TOC was measured using a TOC analyzer (multi N/C 3100, Analytic Jena, Germany) to determine the mineralization. All the experimental data were expressed in terms of arithmetic averages obtained from at least three replicates. The removal efficiency was calculated using Eq. (6):

$$\text{Removal} = \left(\left[\text{concentration}\right]_0 - \frac{\left[\text{concentration}\right]_t}{\left[\text{concentration}\right]_0} \right) \times 100 \qquad (6)$$

where $[\text{concentration}]_0$ and $[\text{concentration}]_t$ denote phenolic compound and TOC concentrations before and after the photocatalytic reaction, respectively.

3. Results and discussion

3.1. Catalyst characteristics

Low-angle XRD patterns for CMK-3 and TiO_2/CMK-3 are represented in Fig. 1. The ordered mesoporous carbon CMK-3 is obtained by the hard template method from SBA-15, which it clarifies that the CMK-3 is an exact replica of the SBA-15 [30]. The CMK-3 and TiO_2/CMK-3 show three peaks for (100),

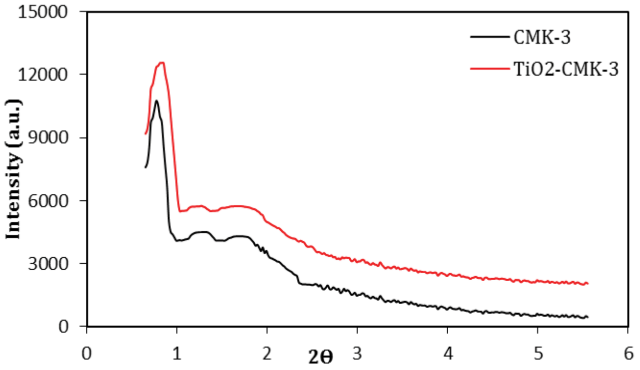

Fig. 1. Small-angle XRD patterns of CMK-3 and TiO_2/CMK-3.

Table 1
Textural properties of CMK-3 and TiO_2/CMK-3 catalysts

	CMK-3	TiO_2/CMK-3
S_{BET} ($m^2\ g^{-1}$)	940.82	875.8
$V_{meso}{}^a$ ($cm^3\ g^{-1}$)	0.78	0.69
V_{micro} ($cm^3\ g^{-1}$)	0.024	0.016
d_0 (nm)	4.86	3.65

$^aV_{meso} = V_{total} - V_{micro}$

(110) and (200) reflections at 2θ less than 2°, which are related to the well-defined 2D hexagonal structure. As it is evident from Fig. 1, there appeared almost no change in the XRD pattern except for the gradual decrease in diffraction intensity of TiO_2/CMK-3 compared with the CMK-3. Fig. 2 shows the adsorption–desorption isotherm N_2 for CMK-3 and TiO_2/CMK-3 samples at 77 K. It can be observed that the adsorption isotherm of both samples was related to the IV isotherm types of the mesoporous material according to the IUPAC classification. Table 1 shows the determined textural properties of the nitrogen physisorption analysis. According to this table, total pore volume (V_t), specific surface area (S_{BET}) and pore size (d_0) of the TiO_2/CMK-3 has decreased compared with CMK-3. This decrease observed is due to the filling of CMK-3 pores by TiO_2 nanoparticles. TEM images of CMK-3 and TiO_2/CMK-3 are shown in Fig. 3. TEM images reveal that both of them are present as a short rod-like morphology. Fig. 3 confirms that the structure order of the TiO_2/CMK-3 is maintained even after introducing TiO_2 nanoparticles in the CMK-3 channels. The TiO_2 nanoparticles appear as dark dot-like objects on the mesopores.

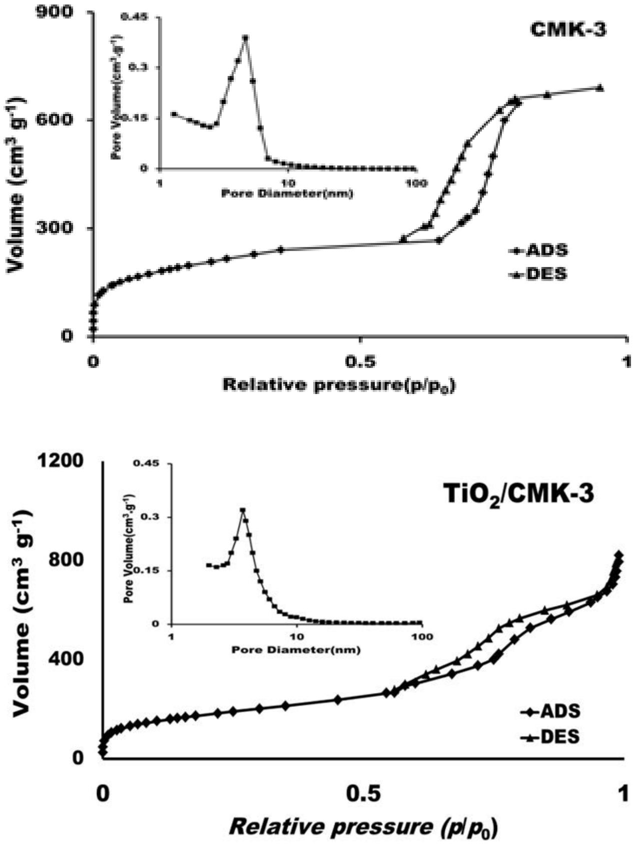

Fig. 2. Nitrogen adsorption–desorption isotherms and pore-size distribution (PSD) for CMK-3 and TiO_2/CMK-3.

3.2. Photocatalytic activity of TiO_2/CMK-3

Before the photocatalytic experiments, a series of batch tests were conducted to accomplish the adsorption–desorption equilibrium behavior among the CMK-3, TiO_2/CMK-3 and phenolic compound under dark condition. As shown in Fig. 4, higher efficiencies were obtained in the photocatalytic processes compared with the adsorption. It was also observed that TiO_2/CMK-3 is more successful than CMK-3 in removing the phenolic compound in the photocatalytic processes. Finally, photocatalytic properties of TiO_2/CMK-3 can be confirmed in phenolic compound removal. Since the performance of photocatalytic degradation depends on the initial solution pH values, initial concentration of pollutant and the concentrations of catalysts, the influence of these parameters on the degradation of phenolic compound in photocatalytic reactions was investigated.

3.2.1. Effect of initial pH

Initial pH is one of the important parameters affecting the photocatalytic degradation of the pollutant due to its effect on the catalyst surface charge, the oxidation potential of the valence band, the adsorption properties and distribution of the adsorbent material [35]. The initial pH effect was investigated on the photocatalytic degradation of phenolic compounds under TiO_2/CMK-3 initial concentration of 0.15 g/L, concentration of 100 mg/L and irradiation time of 150 min and initial pH values from 4 to 10. As shown in Fig. 5(a), the highest degradation efficiency was observed at the pH values between 4 and 6, which means that a slightly acidic and near to neutral environment is more suitable than the alkaline and acidic environments for degradation of the phenolic compounds. Increasing the photocatalytic degradation of phenolic at pH between 4 and 6 can be attributed to the photocatalytic oxidation and adsorption properties. The ionization mode of the photocatalyst surface under acidic and

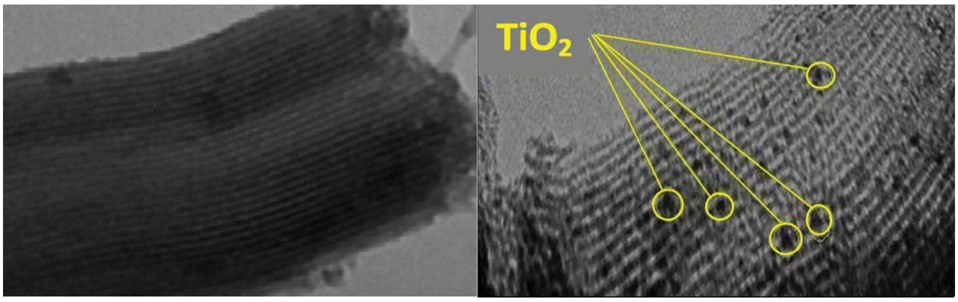

Fig. 3. TEM images of the synthesized CMK-3 and TiO_2/CMK-3.

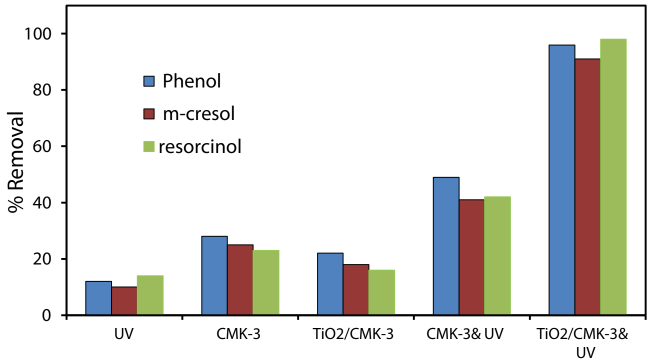

Fig. 4. Removal of phenolic compound under various processes (reaction conditions: pH = 6.0, catalyst (CMK-3 or TiO_2/CMK-3) concentration = 0.15 g/L, phenolic compound = 100 mg/L and reaction time = 150 min).

alkaline conditions, depending on the point of zero charge, can be protonated and deprotonated, as shown in Eqs. (7) and (8). Since the charge zero point (P_{zc}) of TiO_2/CMK-3 is at pH 6.3, In these cases, at the very acidic pH (pH < 3), the phenolic compound molecules and TiO_2 are neutral and the adsorption rate is very low, while by increasing the pH values up to 5 and 6, the surface of TiO_2 is positively charged and the highest adsorption is achieved. At the pH values higher than P_{zc}, the surface of TiO_2 is negatively charged and the degradation efficiency is reduced due to competition between phenolic molecules and the ions of Na^+ and OH^- on the adsorbent surface [36]. In addition, the CMK-3 has a positive surface charge in acidic pH [37], which it, coupled with high pore volume and the high surface of CMK-3, increases the adsorption pollutant. These results are confirmed with the data given in Fig. 5(b). Considering these cases, the high adsorption of phenolic compound on the surface of the TiO_2 and CMK-3 composites provides the chance to increase the photocatalytic degradation by $OH^{\bullet}$ produced by the TiO_2 catalyst under UV irradiation. In some studies, the lowest electron–hole recombination at low pH was also reported as another reason for increasing the efficiency in the heterogeneous photocatalytic [13].

The reductions in the photocatalytic degradation of phenolic compounds in alkaline pH can be due to reducing the catalyst and adsorbent collisions, and the formation of carbonate ions as OH scavenger [13]. Similar results were observed by Zhou et al. [38] in the degradation of orange G from aqueous solutions [38]. In these pH values, the removal of the pollutant is mainly due to the oxidation by $OH^{\bullet}$ produced through Eq. (9). This was proven by the results of the Rajamanickam and Shanthi [39] reports.

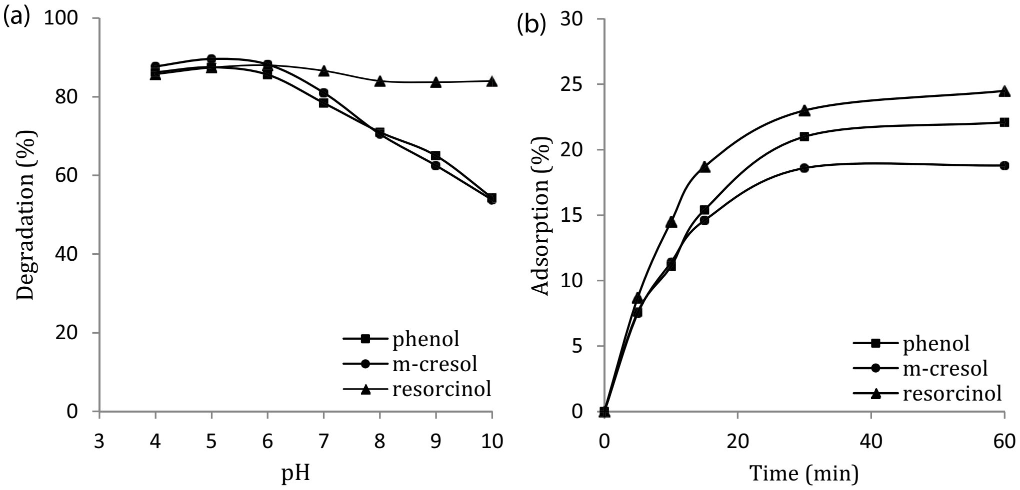

Fig. 5. (a) Effect of initial pH on the degradation efficiency of phenolic compounds (concentration of TiO_2/CMK-3 = 0.15 g/L, phenolic compound concentration = 100 mg/L and irradiation time = 150 min), and (b) Effect of adsorption time on the TiO_2/CMK-3 adsorption efficiency (concentration of TiO_2/CMK-3 = 0.15 g/L, phenolic compound concentration = 100 mg/L and adsorption time = 60 min).

$$\mathrm{pH} < P_{zc} \quad \mathrm{TiO\,H + H^+ \rightarrow TiO\,H^+} \tag{7}$$

$$\mathrm{pH} > P_{zc} \quad \mathrm{TiO\,H + OH^- \rightarrow TiO^+ + H_2O} \tag{8}$$

$$\mathrm{OH^-} + h^+ \rightarrow \mathrm{OH^\bullet} \tag{9}$$

3.2.2. Effect of catalyst concentration

The initial concentration of TiO_2/CMK-3 catalyst on the photocatalytic degradation of phenolic compounds was investigated using the catalyst concentrations in the range of 0.05–0.5 g/L at pH = 6, pollutant concentration of 100 mg/L and irradiation time of 150 min. The photocatalytic activity of TiO_2/CMK-3 gradually improved from 0.05 to 0.15 g/L, as shown in Fig. 6, while, by a further increase (>0.2 g/L), the photocatalytic performance of TiO_2/CMK-3 for degradation of phenolic compounds decreased. Increasing the efficiency at the concentration of 0.15 g/L is mainly due to increasing the number of active sites on the photocatalyst surface for the adsorption and oxidation of the phenolic compound by the production of active radicals [40]. Reducing the efficiency at higher concentrations is related to the scattering of light and the accumulation of particles by collision [13]. Barakat et al. [41] studied the effect of Co-doped TiO_2 concentration (5–35 mg/L) on the 2-CP photocatalytic degradation. The authors found that, by increasing the initial concentration of

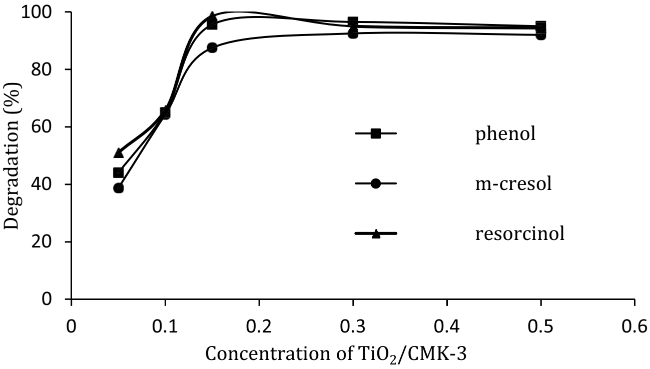

Fig. 6. Effect of initial concentration of TiO_2/CMK-3 on the efficiency of phenolic compounds degradation (pH = 6, phenolic compound concentration = 100 mg/L and irradiation time = 150 min).

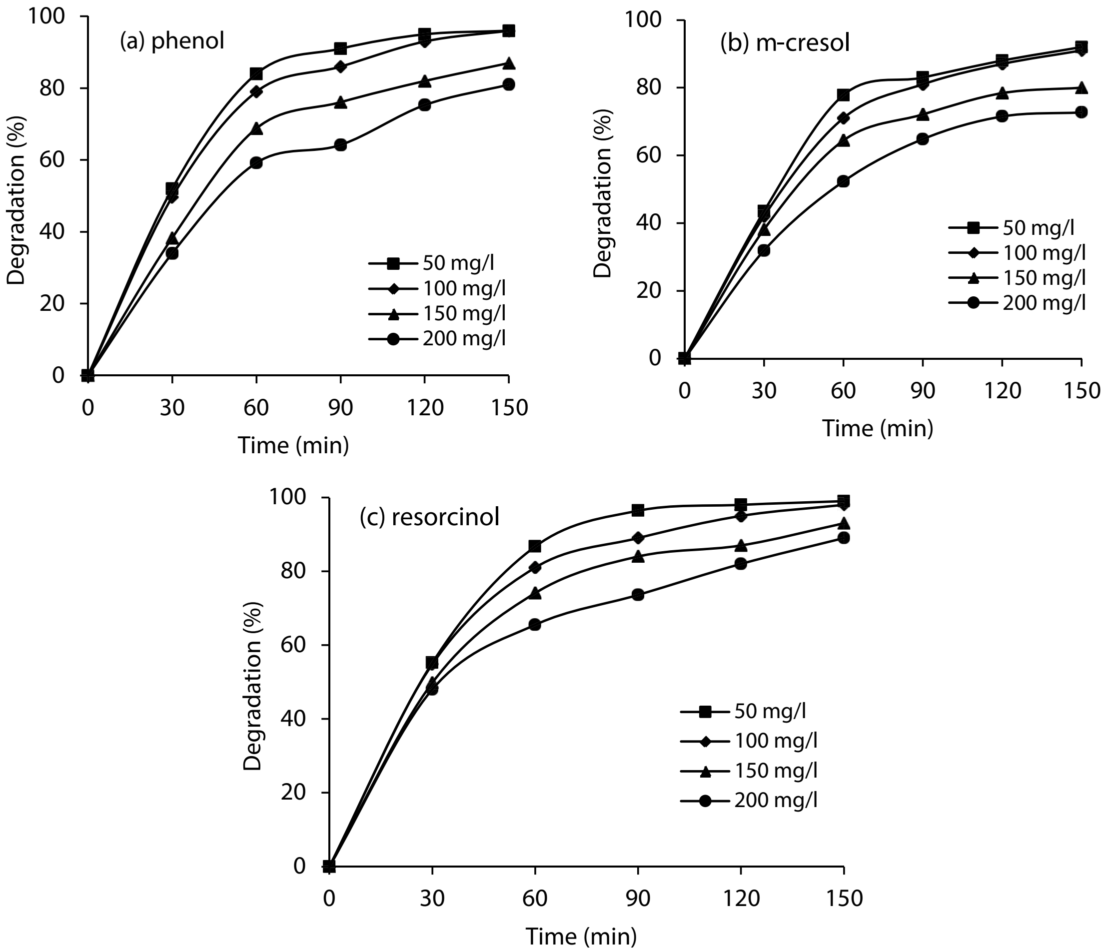

Fig. 7. Effect of initial concentration of phenol compounds on the degradation efficiency of phenol (a), *m*-cresol (b), and resorcinol (c) (pH = 6, concentration of TiO_2/CMK-3 = 0.15 g/L and irradiation time = 150 min).

Table 2
Kinetic constants for the photocatalytic degradation of various concentrations of phenolic compounds

Parameters	k/min^{-1}	R^2
Phenol		
50	0.0223	0.9626
100	0.0213	0.9927
150	0.0135	0.9689
200	0.0108	0.9804
m-Cresol		
50	0.0167	0.9597
100	0.0161	0.9845
150	0.0109	0.9352
200	0.009	0.9504
Resorcinol		
50	0.0321	0.984
100	0.0254	0.9965
150	0.0138	0.9846
200	0.0033	0.8449

the catalyst, the degradation efficiency increased and then it decreased due to light scattering caused by increasing the catalyst concentration [41]. Moreover, similar results were obtained for the photocatalytic degradation of phenol [42] and methyl orange [43] from aqueous solutions.

3.2.3. Effect of initial concentration of phenolic compounds

The effect of the initial concentration of phenolic compounds on photo-degradation has been investigated using different initial concentrations between 50 and 200 mg/L, and the results are shown in Fig. 7. It was found that the efficiency of phenol, *m*-cresol and resorcinol degradation was reduced by increasing the initial concentration of phenolic compounds. This may be due to an increase in the number of molecules of phenolic compounds adsorbed on the TiO_2/CMK-3 surface by increasing the initial concentration of the compounds, which is resulted in the deactivation of the photocatalyst site and further consumption of oxidizing species during the photo-degradation process [44]. Mangrulkar et al. [45] evaluated the photocatalytic degradation of phenolic compounds using N-doped mesoporous titania and found that the phenol and o-chlorophenol degradation efficiency decreased by increasing the initial concentration of these phenolic compounds. The authors explained that, by increasing the initial concentration, the amount of decomposed organic species increased, but the production of reactive species, photocatalyst concentration, intensity and time of illumination remained constant, which it leads to decrease the degradation efficiency [45]. The results are also in agreement with other tasks [46–48].

Degradation kinetics of phenolic compounds as a function of different concentrations of pollutants was investigated according to the first kinetic model ($\ln(C_0/C) = K_t$). According to the results of Table 2, the kinetic constant rate decreases with increasing the initial phenolic compound concentration. This decrease is due to the possibility of interaction between phenolic molecules with active radicals. Similar results were obtained by Rafiee et al. [49] for photocatalytic degradation of phenol by TiO_2/graphene/heteropoly acid nanocomposite.

3.3. Mineralization of phenolic compounds

The mineralization rate of phenolic compounds in the TiO_2/CMK-3 nano-composite system was evaluated by the TOC removal rate. As can be seen, by increasing the irradiation time, the mineralization efficiency is increased for all three phenolic compounds. This increase in the removal of TOC is due to increasing the chance of photocatalytic

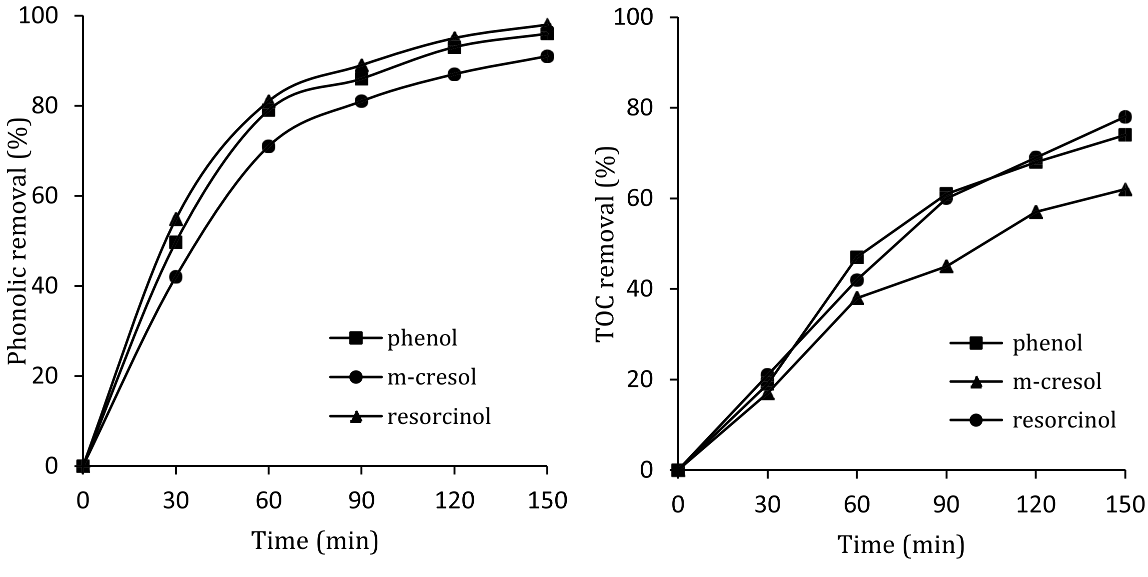

Fig. 8. Removal of TOC and phenolic compounds during photocatalytic process (pH = 6, TiO_2/CMK-3 concentration = 0.15 g/L, phenolic compounds concentration = 100 mg/L and irradiation time = 150 min).

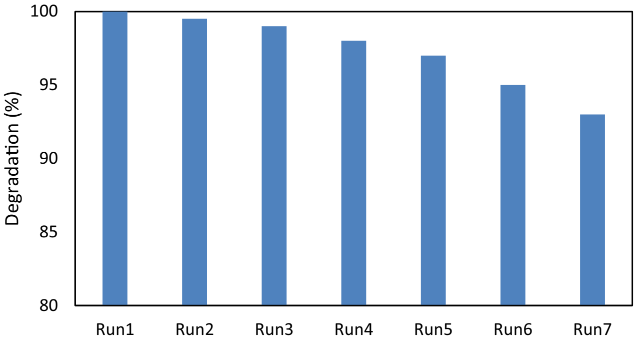

Fig. 9. Phenol degradation in runs of consecutive cycles using regenerated composite TiO_2/CMK-3 as photocatalyst (pH = 6, TiO_2/CMK-3 concentration = 0.15 g/L, phenolic compounds concentration = 100 mg/L and irradiation time = 150 min).

degradation of organic compounds by oxidants produced on the TiO_2/CMK-3 surface. Similar results were observed in the study conducted by Rafiee et al. [49] for the photocatalytic degradation of phenol. Fig. 8 also shows that the TOC degradation rate is lower than the phenolic compounds degradation. This reduction in the removal efficiency of TOC is related to the intermediate products produced in the catalytic reaction.

3.4. Catalyst stability of TiO_2/CMK-3

The photocatalyst stability of TiO_2/CMK-3 was investigated by conducting seven runs of consecutive cycles, as shown in Fig. 9. After each run of phenolic compounds degradation, the catalyst was collected, washed with distilled water and then dried at 60°C in an oven; and, after its regeneration, used in the next run. It can be observed that, after five consecutive runs, the phenol removal efficiency is reduced to 95%, which indicates that the reduction of TiO_2/CMK-3 catalytic activity was insignificant. A lower reduction in the degradation efficiency can be due to reducing the concentration of TiO_2/CMK-3 catalyst and destruction of catalytic active sites by the adsorbed intermediate products. Similar results were observed by Jiang et al. [43] for the degradation of methylene orange dye using TiO_2/carbon nanotubes photocatalyst. The authors reported that the reduction of degradation efficiency in consecutive cycles is related to reducing the photocatalyst through the filtration and washing in the regeneration process [43].

4. Conclusion

In this study, the TiO_2/CMK-3 nanocatalyst composite was prepared by combining CMK-3 synthesized using the SBA-15 and titanium(IV) isopropoxide and it was then used as the catalyst for the photocatalytic degradation of phenol, *m*-cresol and resorcinol. Analysis of XRD, TEM and N_2 adsorption–desorption revealed the successful incorporation of TiO_2 into the CMK-3 structure. The photocatalytic degradation efficiency of phenolic compounds was strongly influenced by pH, catalyst concentration, initial concentration of pollutant and irradiation time. At the optimum condition obtained (pH = 6, TiO_2/CMK-3 concentration of 0.15 g/L, phenolic compounds concentration of 100 mg/L and irradiation time of 150 min), the phenol, *m*-cresol and resorcinol degradation efficiency was obtained to be 96%, 91%, and 98% and the TOC removal efficiency was observed to be 74%, 62%, and 78%, respectively. This high efficiency is related to the large surface area provided by mesoporous CMK-3 and the placement of TiO_2 into the CMK-3. The TiO_2/CMK-3 composite showed the excellent long-term stability and reusability. As a result, the nanocatalyst TiO_2/CMK-3 can be used as a promising photocatalyst for the photocatalytic degradation of phenolic compounds.

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