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Removing Chlorobenzene via the Synergistic Effects of Adsorption and Catalytic Oxidation over Activated Carbon Fiber Loaded with Transition Metal Oxides

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Abstract: This study focused on the elimination of chlorobenzene by dual adsorption/catalytic oxidation over activated carbon fibers (ACFs) loaded with transition metal oxides (TMOs). The TMOs were successfully loaded on the ACFs by the incipient wetness impregnation method, which has the advantages of easy preparation, low cost, and size uniformity. The removal effects for chlorobenzene (CB) were investigated on pristine ACFs and TMOs@ACFs in a fix-bed reactor. The adsorption/catalytic oxidation experiments result demonstrated that ACFs can be used as a very efficient adsorbent for the removal of low-concentration CB at the low temperature of 120 °C; the breakthrough time of CB over pristine ACFs can reach 15 h at an inlet concentration of 5000 ppmv and space velocity of 20,000 h⁻¹. As the bed temperature rose above 175 °C, the CB removal mainly contributed to the catalytic oxidation of MnO₂; a preferable CB removal ratio was achieved at higher temperatures in the presence of more MnO₂. Therefore, CB can be effectively removed by the dual adsorbent/catalyst of MnO₂@ACF at the full temperature range below 300 °C.

Keywords: chlorobenzene removal; activated carbon fibers; MnO₂; adsorption; catalytic oxidation



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1. Introduction

Volatile organic compounds (VOCs) are the main air pollutants involved in atmospheric photochemical reactions [1]. Especially, chlorinated VOCs (CVOs) are highly toxic and quite difficult to deal with due to the presence of chlorine and their diversities varying from low molecular weight (CHCl₃, CH₂Cl₂, and chlorobenzene (CBs)) to polymers of PCBs and polychlorinated dibenzodioxins (PCDDs). CVOs have to be properly treated, for they are widely used in various industries and detected in the environment, which causes grievous harm to human health and the environment [2,3]. CB, a simple chloroaromatic hydrocarbon, is a key chemical and pharmaceutical intermediate and an important precursor of PCDDs [4], which has been recognized as a model pollutant to evaluate the removal effect of CVOs.

During the past decades, many methods have been developed to remove CB, i.e., absorption, membrane separation, photocatalytic degradation, adsorption, catalytic combustion [5–7], etc. Among these technologies, adsorption and catalytic combustion have gained much popularity. Adsorption has prominent advantages, such as high efficiency, easy operation, and low cost, so it has been extensively employed to remove VOCs and other air pollutants [8–10]. A variety of adsorbents, including biochar [11], activated carbon (AC) [12–14], carbon nanotubes [15], and biomass-based nanofiber [16], have been used to remove CB via adsorption. Comparatively speaking, AC possesses a large specific surface area and high porosity, sufficient surface functional groups, and excellent chemical stability, thus, AC is an ideal adsorbent for organic pollutants, showing obvious advantages in the adsorption of VOCs. A lot of flue gases in industrial processes contain VOCs at low concentrations (about

200 ppm) [17]; therefore, AC is a perfect choice for their removal. However, adsorption removal is weakened at higher temperatures, and the adsorption process is usually exothermic. The adsorption will eventually be saturated, so it is hard to remove VOCs merely by adsorption with high concentrations at high temperatures in practical application.

Besides adsorption, catalytic oxidation is a promising and emerging technology for the removal of VOCs that has lower energy requirements and low capital costs. More interestingly, catalytic oxidation is highly effective in the temperature range of 250 to 500 °C and can deeply oxidize and completely degrade CB into harmless gases (H_2O , CO , and CO_2) and readily removable combustion products (Cl_2 , HCl). The CVOC removal effect via catalytic oxidation is dominantly dependent on the suitable catalysts, which should have strong oxidizing capabilities and high selectivity for HCl and CO_2 . Tremendous efforts have been devoted to the design, fabrication, and testing of proper catalysts. In general, there are three kinds of catalysts, such as noble metals, zeolites, and transition metal oxides. Although noble metal catalysts exhibit the highest activity, they are prone to Cl poisoning, sintering, and leaching [18,19]. Zeolites (H-EBA [20], H-ZSM-5 [21]) present considerable catalytic activity due to their large specific surface area and abundant acidity, but the resulting coke deposition is difficult to avoid, so their applications are greatly limited.

Compared with noble metals and zeolites, transition metal oxides (TMOs) possess excellent thermal stability, a lower cost, and a stronger toxic resistance capability; many TMOs have been fabricated as catalysts in the catalytic oxidation of CB, for example, CeO_2 [22], MnO_2 [23], Fe_2O_3 [24], TiO_2 [25], etc. Among them, Ce-containing TMOs have received much attention as catalysts for CB oxidation due to their remarkable redox properties, high oxygen storage capacity, sufficient oxygen vacancies, and excellent dissociating C–Cl bonds [26]. Nevertheless, CeO_2 -based catalysts are vulnerable to deactivation due to the strong adsorption of Cl species produced from the degradation of CB [27]. Manganese oxides are recognized as one of the most efficient catalysts for CVOC oxidation due to the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox cycle, showing superior catalytic activity with prominent oxygen availability and mobility [28]. However, manganese oxides are also susceptible to Cl poisoning, for the adsorbed Cl species will reduce oxygen mobility [29]. Unfortunately, these catalysts almost always play roles at a higher temperature from 250 to 500 °C, they are unable to remove CVOCs at a temperature below 200 °C. Additionally, agglomeration usually occurred for TMO powder catalysts, which decreased their activity and CVOC removal performance.

In recent years, dual functional adsorbents/catalysts with excellent adsorption and catalytic functions were proposed as a more effective control method for disposing of VOCs [30,31], combining the advantages of adsorption and catalytic oxidation techniques. Great efforts have been devoted to obtaining new materials that could facilitate the adsorption/oxidation processes. Activated carbon fibers (ACFs) show high adsorption capacity and catalytic oxidation capability due to their high surface area, porosity, and unique surface chemistry characteristics [32]. ACFs loaded with proper catalysts, such as MnO_2 , can be used in the catalytic oxidation of formaldehyde [33] and NO [34] with higher activity. To the best of our knowledge, little research has focused on the design of dual adsorption/catalytic oxidation catalysts for the removal of CVOCs. Herein, we aimed at developing an effective dual adsorbent/catalyst for the removal of CB, which is expected to have a high-efficiency removal effect for CB under low temperatures. Based on the abovementioned merits of ACF and TMOs, ACF was selected as the adsorbent and catalyst carrier, and three different kinds of TMOs were loaded onto the ACF by the incipient wetness impregnation method to produce a $\text{MO}_x@\text{ACF}$ dual functional adsorbent/catalyst. The pristine ACF and as-prepared $\text{MO}_x@\text{ACF}$ were used to remove CB, and the CB removal effect under different operation conditions was investigated. This study may open a new way to remove CVOCs by dual functions of adsorption and catalytic oxidation.

2. Materials and Methods

2.1. Materials and Catalysts Preparation

ACF was offered by Osaka Gas Co., Ltd. (Osaka, Japan). Manganese (II) acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 99%), Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), ammonium metavanadate (NH_4VO_3), and nitric acid were purchased from Beijing Modern Fine Chemical Co., Ltd., which were all analytically pure.

The transition metal oxides loaded on ACF ($\text{MO}_x\text{@ACFN}$) catalysts were prepared by incipient wetness impregnation method, in which the treated ACF with nitric acid (ACFN) was used as the catalysts support. The preparation process is illustrated in Figure 1. A typical process is as follows: A certain weight of ACF (2.0 g) was cleaned with deionized (DI) water and dried for 24 h at 100 °C then soaked in a premade dilute nitric acid (30 wt%) solution (64 mL) for some time under moderate stirring. The mixture of ACF and acid solution were heated to 80 °C under vigorous stirring for 2 h. The treated ACF was obtained after rinsing with DI water until neutral and dried at 150 °C overnight, labeled as ACFN. To prepare $\text{MO}_x\text{@ACFN}$, a certain amount of metal salts, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.2327 g), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.1617 g), and NH_4VO_3 (0.1198 g) were weighed, respectively, and they were dissolved with 12 mL DI water in beakers forming into salts solution. Later, 0.60 g ACFN was added into the above salts solution and sealed with plastic wraps; they were firstly stirred for 2 h under heating followed by standing for 12 h to let metal salts load onto the supports. After the incipient wetness impregnation process, the solvents were evaporated under water bath and the impregnated products were further dried at 105 °C. Finally, the dried metal salts@ACFN were sintered at 500 °C for 3 h at the heating rate of 5 °C/min under N_2 .

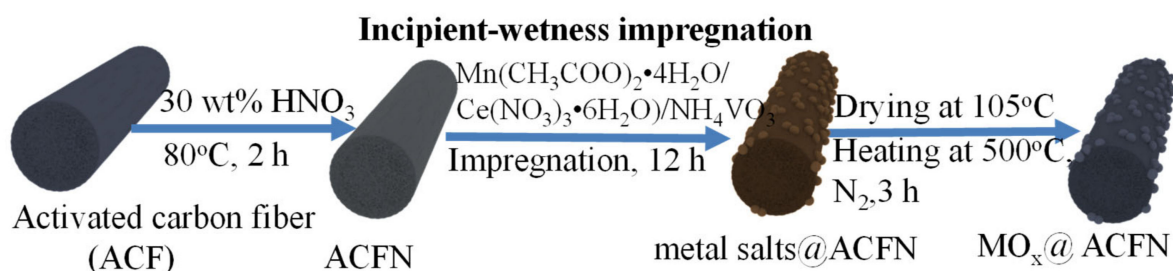


Figure 1. Preparation process of metal oxides@ACFN catalysts via incipient wetness impregnation method.

2.2. Catalysts Characterization

Scanning electron microscopy (SEM) images were used to observe the surface morphologies of the ACF and $\text{MO}_x\text{@ACFN}$ catalysts, which were obtained on an LEO-1530 microscope. The X-ray diffraction (XRD) patterns were recorded on a powder diffractometer (X'Pert PW3050/60) using $\text{Cu K}\alpha$ radiation (40 kV and 40 mA); the scattering rate was 5 °/min, and the scattering angles (2θ) ranged from 10 to 80°. The Raman spectra were acquired on Lab Ram HR800. Nitrogen adsorption and desorption isotherms were collected on Belsorp instruments (BelMax, Bel JAPAN inc., Osaka, Japan). The specific surface area of ACF was calculated using Brunauer–Emmett–Teller (BET) method, and the pore volumes and pore size distributions were determined using nonlocal density function theory (NLDFT) [35].

2.3. Experimental Setup for Chlorobenzene Removal

The experimental setup is displayed in Figure 2. The feed gases consisted of nitrogen, oxygen, and CB stream carried with nitrogen, whose flow rates were all regulated by gas mass flow controller (MFC) (Seven-star DF07-26C). The three gas streams were blended in a gas mixer. The homogenized mixture gases went across a fixed catalytic bed inside a tubular quartz reactor, which was surrounded and heated in a convective flow oven. After adsorption/oxidation, the resultant gases were dried with a permeation system filled with

CaCl_2 and finally analyzed with an online analysis system. The online gas chromatograph (Shimadzu GC-2014C, Shimadzu, Kyoto, Japan) was equipped with a hydrogen flame ionization detector (FID) and PEG-6000 capillary column.

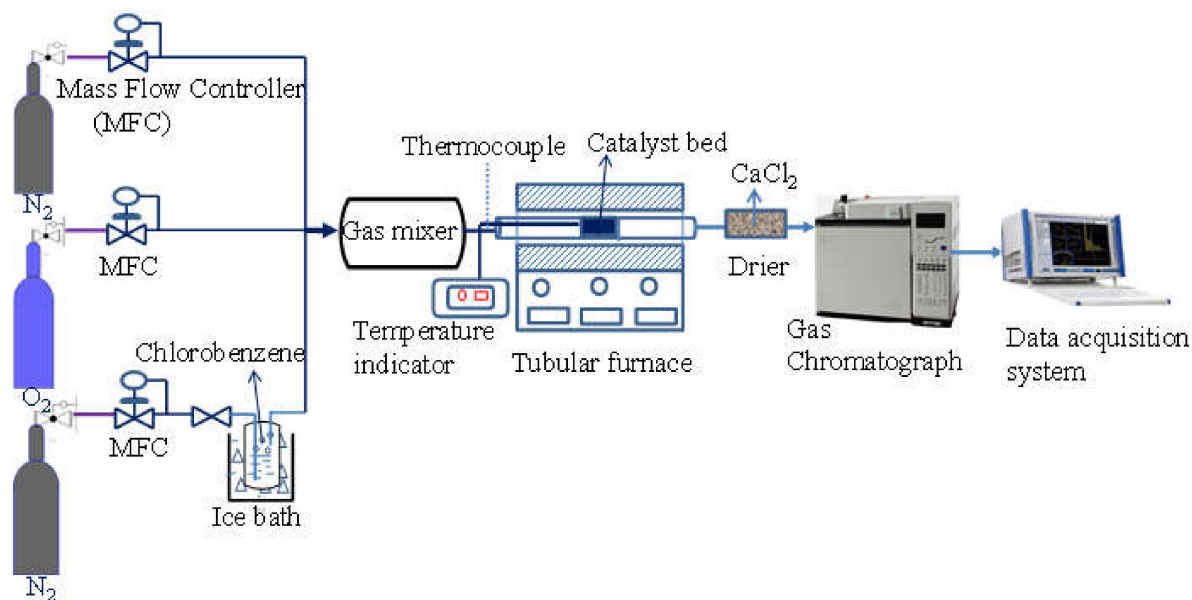


Figure 2. The experimental set-up for the adsorption/catalytic oxidation of chlorobenzene.

2.4. Chlorobenzene Adsorption and Catalytic Oxidation Tests

The adsorption and catalytic oxidation of CB on ACF or $\text{MO}_x\text{@ACFNs}$ were tested in a continuous flow microreactor, which constituted a quartz tube reactor with an inner diameter of 8 mm shown at atmospheric pressure in Figure 2. The pristine ACF and as-prepared metal oxides@ACF were used as adsorbents/catalysts for removing CB. A 0.1 g sample of the catalyst was loaded at the center of the reactor for each experiment. CB was introduced into the reactor by blowing liquid CB maintained at 0 °C with dry N_2 as the carrier gas, and its concentration was controlled by adjusting the flow rate of the carrier gas N_2 metered by an MFC. The feed gas into the reactor was generated by mixing CB with dry N_2 and O_2 in a gas mixer which consisted of 21 vol% O_2 and a balance of N_2 . The total gas flow rate was controlled at 100 mL/min at standard state (SCCM), and the gaseous hourly space velocity (GHSV) was approximately $20,000 \text{ h}^{-1}$. The adsorption performance of the pristine ACFs for CB was measured over the temperature range of 100–200 °C with different CB inlet concentrations. The catalytic oxidation activities of the $\text{MO}_x\text{@ACFNs}$ were investigated at 100–350 °C, and the temperature was controlled by the tube furnace and measured with a thermocouple into the center of the reactor. The effluent gases were analyzed at a given temperature using an online gas chromatograph (GC) equipped with an FID for the quantitative analysis of CB.

3. Results and Discussions

Adsorbent and catalyst supports should possess high CVOC adsorption capacities, so the adsorption capacity of the pristine ACF was first evaluated. Then, the catalytic oxidation over various transition metal oxides loaded with ACFN ($\text{MO}_x\text{@ACFN}$) was carried out to ascertain the most active TMO catalyst and the entire transformation temperature of the CB. Finally, adsorption/catalytic oxidation tests over the optimal $\text{MO}_x\text{@ACFN}$ with different loaded amounts were performed in order to determine the proper loaded amount of TMO. All the experiments were conducted in the same reactor shown in Figure 2.

3.1. Adsorbent/Catalysts Characterizations

Figure 3 displays the SEM micrograph, Raman spectrum, XRD pattern, nitrogen adsorption–desorption isotherms, and pore size distributions (PSDs) of the pristine ACFs. Figure 3a and the inset show the morphology of the ACFs after they were rinsed with deionized water. As observed, the pristine ACFs exhibited a one-dimensional, rod-like structure with typical mean diameters of about 10 μm , which are evenly distributed. Moreover, their surface looked very clean and smooth with few impurities. Figure 3b shows the Raman spectrum of the ACFs examined in this study. The spectrum possessed two main characteristic bands around 1347 and 1601 cm^{-1} , which are attributed to the so-called D and G bands of carbon materials, respectively. The D band was ascribed to the disorder-induced lattice distortion or the sp^3 -hybridized amorphous carbon while the G band was associated with the sp^2 -hybridized graphitic carbon [36–38]. Thus, the intensity ratio (I_D/I_G) of the D and G bands can indicate the graphitization degree of the ACF; the calculated I_D/I_G was 1.10, indicative of some amorphous structure.

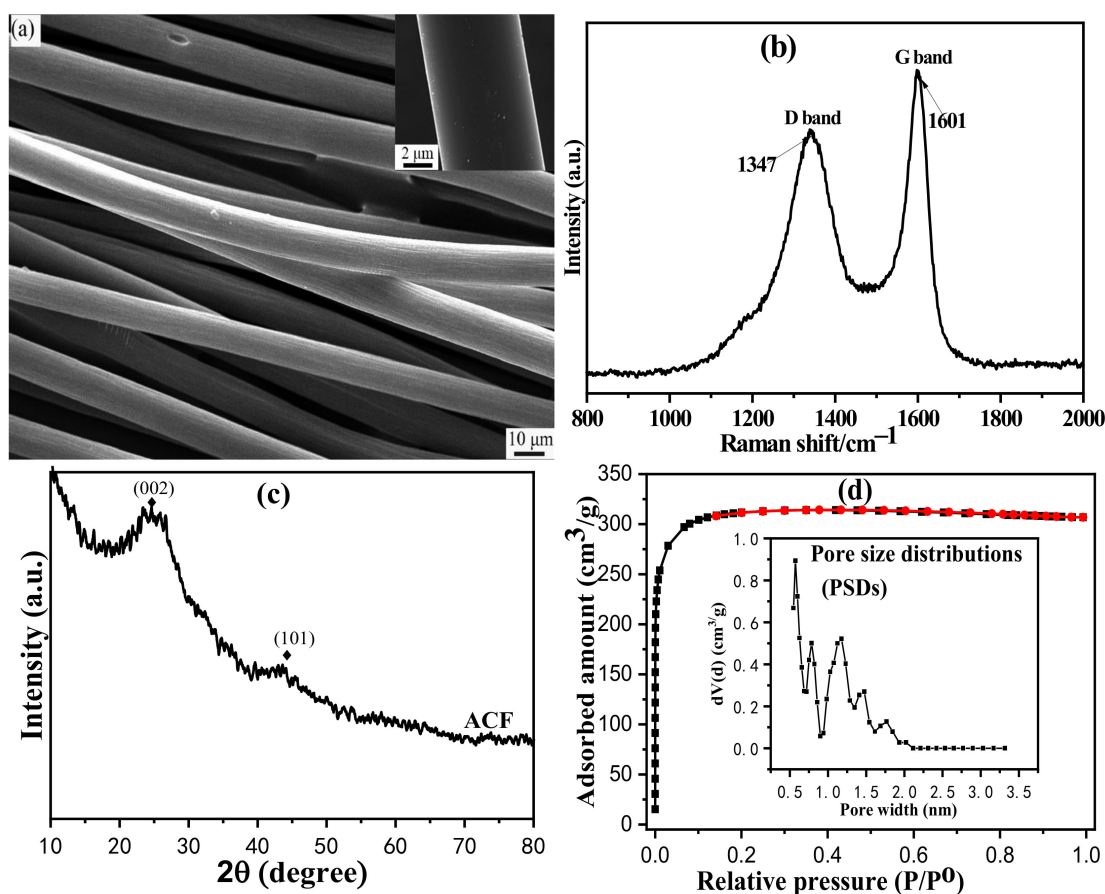


Figure 3. Characterizations of the pristine ACF, (a) SEM micrograph, (b) Raman spectrum, (c) XRD pattern, (d) nitrogen adsorption/desorption isotherm curves, and pore size distributions (PSDs).

The XRD pattern is depicted in Figure 3c. ACF is usually an amorphous carbon which is composed of random microcrystalline carbon fragments, including single reticular planes and nonorganized carbon as well as graphite-like microcrystals. The XRD pattern showed broad and stronger diffraction peaks centered at $2\theta = 25.1^\circ$ and a weak peak at $2\theta = 43.2^\circ$, corresponding to the (002) and (101) crystal planes of carbon [39], respectively. The N_2 adsorption/desorption isotherm curve of ACF is shown in Figure 3d. The pristine ACF exhibited the type-I adsorption/desorption isotherm according to the International Union of Pure and Applied Chemistry (IUPAC) classification [40,41]. As seen from the isotherm, sharp adsorption was observed in the very low relative pressure range (P/P^0) of 0.1, and a

nearly horizontal plateau was almost attained at P/P^0 of 0.2 until the high relative pressure (1.0). Moreover, the desorption branch was practically superimposed on the adsorption branch. These indicated that micropores contributed dominantly to the porosity of the ACF. Based on the N_2 adsorption/desorption isotherms, the calculated PSDs by NLDFT were illustrated in the Figure 3d inset, which confirmed that the pristine ACF contains a large number of micropores with the pores almost all in the range of 0.5–2.0 nm. The specific surface area by BET, total pore volume (V_{total}), and micropore volume (V_{micro}) were $1174 \text{ m}^2/\text{g}$, 0.46 , and $0.42 \text{ cm}^3/\text{g}$, respectively. Such a structure that possesses a high surface area and abundant micropores is very beneficial to the adsorption of chlorobenzene and loading catalysts over ACF.

The SEM images of treated ACF with HNO_3 and $MO_x@ACFN$ are presented in Figure 4. Compared with the clean surface of the pristine ACF, the surface of the ACFN became rough and uneven with some cracks, which was beneficial to the loading of metal oxides. As mentioned above, ACFs provide a high surface area, helping the dispersion of the catalysts on the fiber surface. After immersing the ACFN into the metal salt solution for some time, metal oxides were coated on the ACFN by the incipient wetness impregnation method. The SEM images shown in Figure 4b–d confirmed that the transition metal oxides were successfully loaded onto the ACFN. It is easily observed that some fine metal oxide nanoparticles (NPs) were dispersed on the fiber surface, and they were proved to be MnO_2 by XRD analyses. Obviously, with the increase of the loading amount of MnO_2 from 5 to 8 to 10 wt%, there were more and more NPs on the ACFN. Especially when the mass ratio of MnO_2 to ACF was 10 wt%, the NPs became dense and clustering or aggregation occurred.

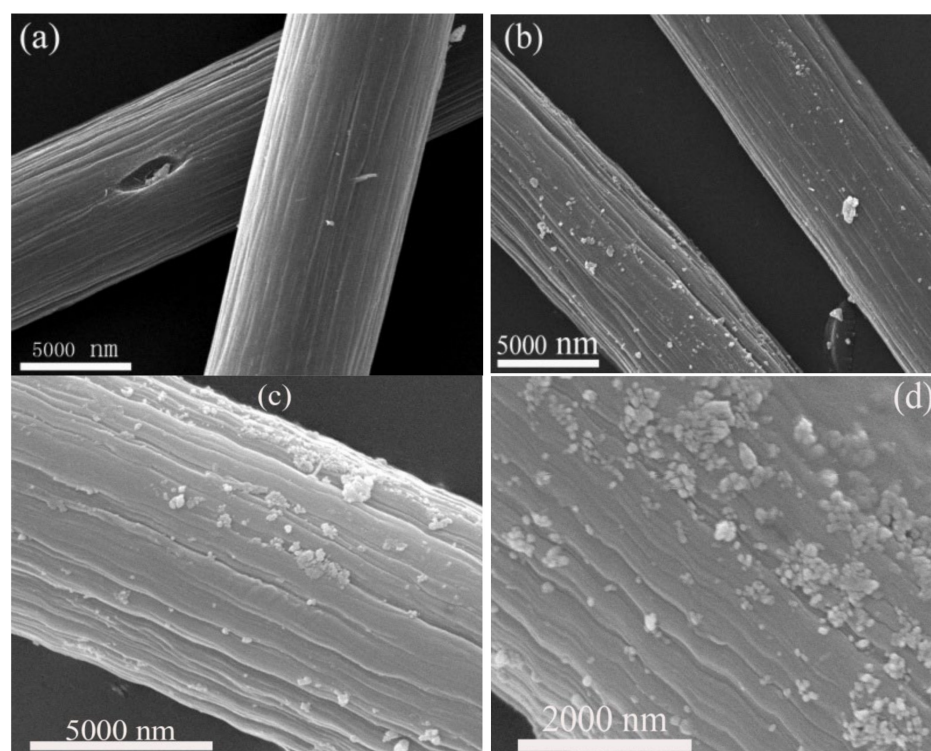


Figure 4. SEM image of ACFN (a) and ACFN with loading different MnO_2 amounts: (b) 5 wt%, (c) 8 wt%, and (d) 10 wt%.

Structural analysis of the fabricated materials was characterized using XRD and illustrated in Figure 5. Consistent with the pristine ACF, the XRD pattern of the composite also exhibited two typical peaks at around 25° and 43° , corresponding to (002) and overlapping (10) reflection from (100) and (101) planes, respectively, which are attributed to the carbon. In addition to the two peaks, there were another three peaks located at 28.75° , 37.46° , and

59.54°, which can be indexed to the (110), (101), and (220) planes of MnO₂ (JSPDS card NO. 72-1984). The XRD results confirmed the coexistence of MnO₂ and carbon.

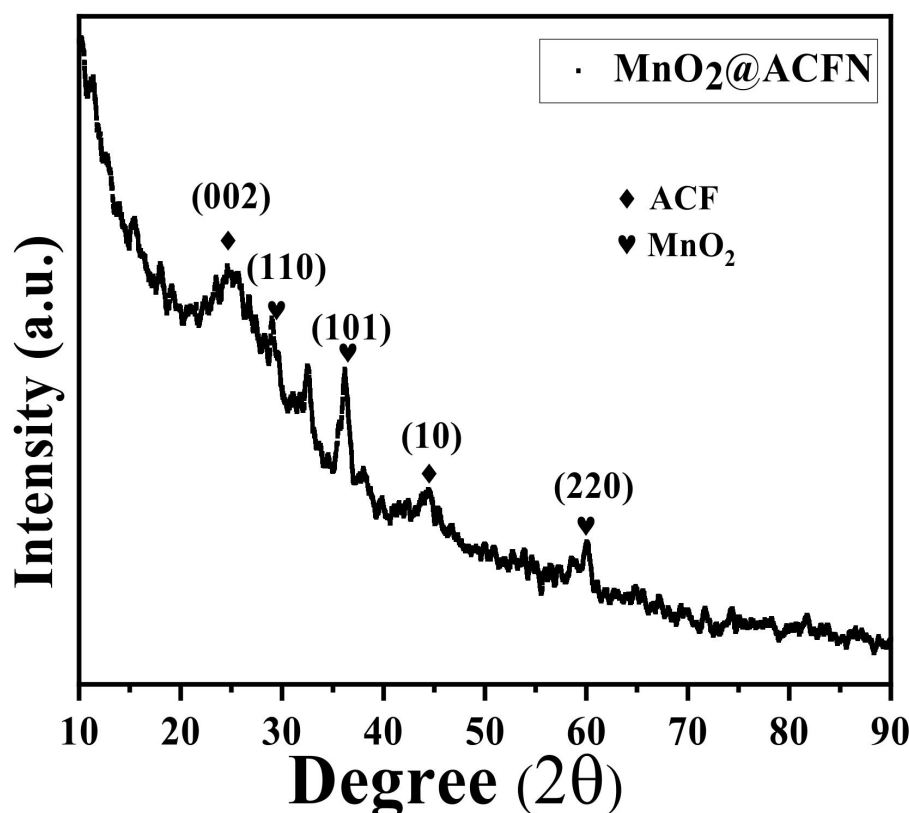


Figure 5. XRD patterns of MnO₂@ACFN.

3.2. Adsorption of CB over the Pristine ACF

In order to examine the removal effect of pristine ACF for CB by adsorption only, the adsorption experiments were performed on the setup shown in Figure 2. Firstly, the experiments were conducted at different bed temperatures at 120, 150, 175, and 200 °C to investigate the effect of the temperature on the adsorption of CVOC. For all test runs, the inlet concentration of CB was kept constant at 5000 ppm, the mass of the pristine ACF samples was 0.1 g, and the gas flow rate was a controlled constant of 100 SCCM by MFC. The experimental breakthrough curves of CB adsorption over ACF were obtained at four different temperatures and depicted in Figure 6. Breakthrough curves give the dimensionless concentration (C_{outlet}/C_{inlet}) as a function of time at the outlet of the fix-bed reactor. In general, the dynamic adsorption capacity (q , mg•g^{−1}) of the adsorbent was calculated by Equation (1) [42,43] based on the breakthrough curve

$$q = \frac{V}{M} \int_0^t (C_{inlet} - C_{outlet}) dt \quad (1)$$

where C_{inlet} (mg•L^{−1}) and C_{outlet} (mg•L^{−1}) represent the concentrations of CB in the gas at the inlet and outlet, respectively; V (L•min^{−1}) is the volumetric gas flow rate; M (g) is the mass of adsorbent (ACF); and t (min) denotes the adsorption time.

As shown in Figure 6, there were sharp rise stages in the CB concentration after the breakthrough for all the adsorption temperatures, and the breakthrough curves became steeper and steeper with an increase in the adsorption temperature. In addition, the breakthrough time also decreased significantly with an increase in the bed temperature. As seen from the figure, the breakthrough curve shifted to the left when the bed temperature was raised to 200 °C, indicating an early saturation of the bed. The breakthrough time can

run as long as 15 h at 120 °C, but it decreased to 2.5 h at 150 °C. By further increasing the temperature to 175 and 200 °C, the breakthrough occurred almost instantly. As a matter of fact, as the temperature rose to 200 °C, nearly no adsorption happened, leading to a sharp rising breakthrough curve. According to Equation (1), the calculated adsorption capacity of CB over ACF at 120, 150, 175, and 200 °C was 628.35, 172.2, 77.1, and 22.5 mg/g, respectively. This demonstrates that the CB adsorption over ACF was exothermic and extremely sensitive to temperature. The decreases in the breakthrough time and adsorption capacity were ascribed to the enhanced overall mass transfer coefficient at higher temperatures and the exothermic adsorption characteristics. The adsorption process agrees well with previous VOC adsorption studies [44,45]. Although the adsorption capacity at 200 °C was low, it was very high at 120 °C. Previous studies usually investigated the adsorption performance of VOCs under temperatures below 100 °C. These results demonstrated that ACF still had a considerable adsorption capacity for CB at a higher temperature, so it is expected to be feasible to remove CVOCs by adsorption only on ACF.

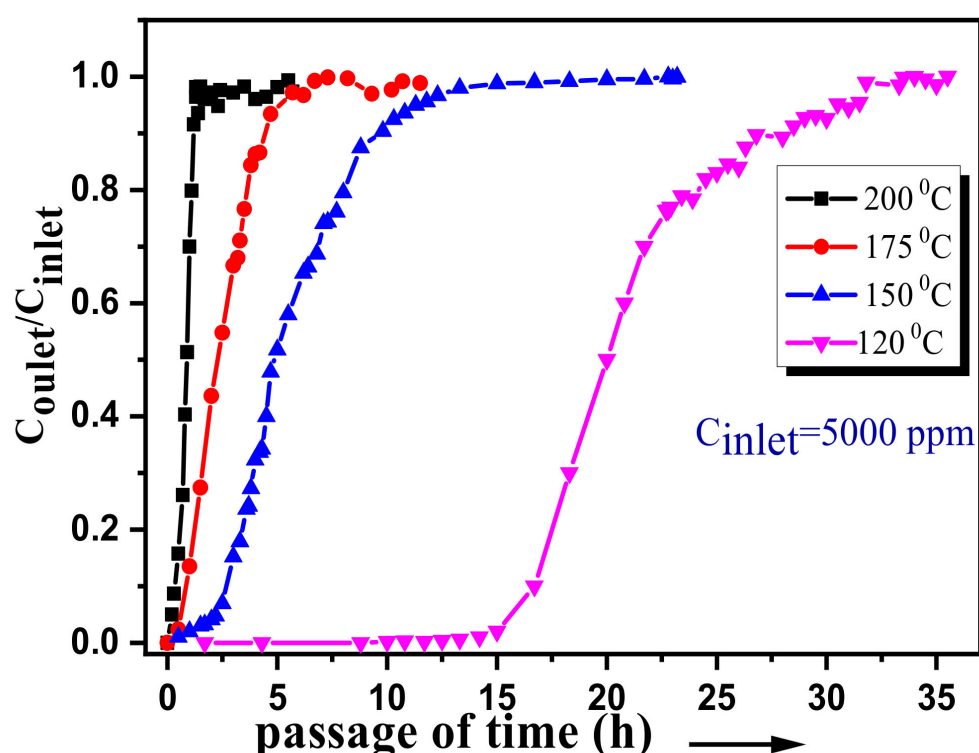


Figure 6. The experimental breakthrough curves of CB adsorption over the pristine ACF at various temperatures from 120 to 200 °C. Tests carried out with 0.10 g ACF, 5000 ppm of initial CB/N₂ concentration, gas flow rate of 100 SCCM, and GHSV = 20,000 h^{−1}.

The inlet concentration of VOCs also had important effects on the adsorption performance of the adsorbent. To check the effects of CVOC initial concentration on the breakthrough characteristics, the adsorption tests were performed for different CVOC inlet concentrations: 5000, 8000, and 11,000 ppm. In each test, 0.1 g ACF was used, the bed temperature was controlled at the predetermined maximum adsorption temperature of 120 °C, and the gas flow rate was 100 SCCM. Figure 7 shows the experimentally obtained breakthrough curves for CB adsorption over ACF with various gas inlet concentrations.

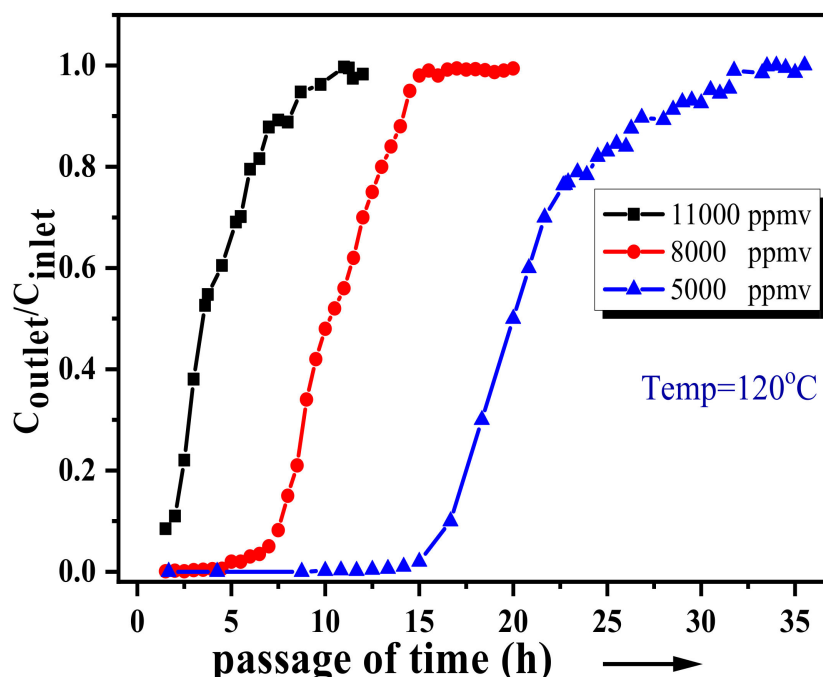


Figure 7. Experimental breakthrough curves at different CB/N₂ inlet concentrations. Experiments conducted at 120 °C, 0.1 g ACF, 100 SCCM gas flow rate, and GHSV = 20,000 h^{−1}.

As observed from Figure 7, the breakthrough curve turned steeper, and the breakthrough time became shorter with the increase in CB inlet concentration. Specifically, the breakthrough time decreased from 15 to 6.5 to 1.5 h as the inlet CB concentration increased from 5000 to 8000 to 11,000 ppm, and the corresponding adsorption capacity moderately decreased from 628.35 to 507.21 to 281.62 mg/g. The decrease in the breakthrough and total adsorption time and the increase in the inlet concentration of CB was ascribed to the effect of the total amount of VOC. Firstly, a greater number of CVOC molecules were impelled to enter the macropores of the ACFs at higher inlet CVOC concentrations under identical gas flow rates [46], leading to a higher adsorption rate. Secondly, the higher inlet VOC concentration meant an increased concentration gradient (driving force), so the overall mass transfer coefficient became larger and the axial dispersion coefficient smaller, resulting in higher values of the kinetic constant [47]. Thus, the saturation of the ACF bed was accelerated in relatively less time due to the higher CB mass flow. The results demonstrated that ACF has an excellent adsorption capacity for CB even at a higher temperature of 120 °C and higher concentration of 5000 ppmv.

3.3. CB Removal by Adsorption/Oxidation

Generally speaking, catalytic oxidation is an effective method to remove VOCs, for it can completely degrade VOCs into harmless molecules, but it is not economically feasible sometimes in the removal of low-concentration VOCs. Integrating the adsorption process with catalytic oxidation will be more effective for the treatment of low-concentration VOCs [48]. As described above, the adsorption experiments confirmed that pristine ACFs have a high adsorption capacity for CB. By loading catalysts (TMO) onto ACF, MO_x@ACF is expected to have a dual adsorption/catalytic oxidation function in removing CVOCs. The dual functional adsorbent/catalyst (MO_x@ACF) experiments were also carried out in the setup in Figure 2, where the CB concentration was 5000 ppm, and 0.1 g composite catalysts were placed into the quartz reactor. The breakthrough time was 2.5 h at 150 °C, and the fixed-bed reactor temperature was increased at a rate of 5 °C/min to the target temperature and kept at 3 h at each specified temperature.

Figure 8 shows the CB removal curves by adsorption/catalytic oxidation over different catalysts. It was found: (1) at a low temperature, adsorption played the dominant role in the removal of CB. The CB removal ratio still reached up to 65% for all the adsorbent/catalysts until 150 °C. (2) With the increase in reactor temperature, the CB removal over the pristine ACF decreased for all times. The CB was removed over the pristine ACF mainly by physical adsorption that is adverse at high temperature while it decreased initially until 180 °C then increased over the $\text{MO}_x\text{/ACF}$ composite catalysts. (3) Among the three catalysts of $\text{VO}_x\text{/ACF}$, $\text{CeO}_2\text{/ACF}$, and $\text{MnO}_2\text{/ACF}$, $\text{MnO}_2\text{/ACF}$ was the most efficient catalyst for the removal of CB via adsorption/catalytic oxidation. It can be seen that $\text{MnO}_2\text{/ACF}$ exhibited catalytic oxidation activity at 180 °C when the CB removal ratio (>50%) was higher than others. During all temperature ranges, the CB removal ratio over $\text{MnO}_2\text{/ACF}$ was always the highest one. The T90 was only 240 °C, which was lower than most of the reported TMO catalysts [49]. For $\text{VO}_x\text{/ACF}$ and $\text{CeO}_2\text{/ACF}$, they exhibited obvious oxidation activity until 270 °C, and the CB removal ratio did not reach up to 90% in the tested temperature. For the $\text{MO}_x\text{/ACF}$ under all the temperatures, the CB removal ratio exceeded 40% while it decreased straightly after 150 °C for the pristine ACF. These results demonstrated that $\text{MO}_x\text{/ACF}$ composites indeed functioned as adsorbents and catalysts for the removal of CB, aiding the adsorption role of ACF and catalytic oxidation of TMOs.

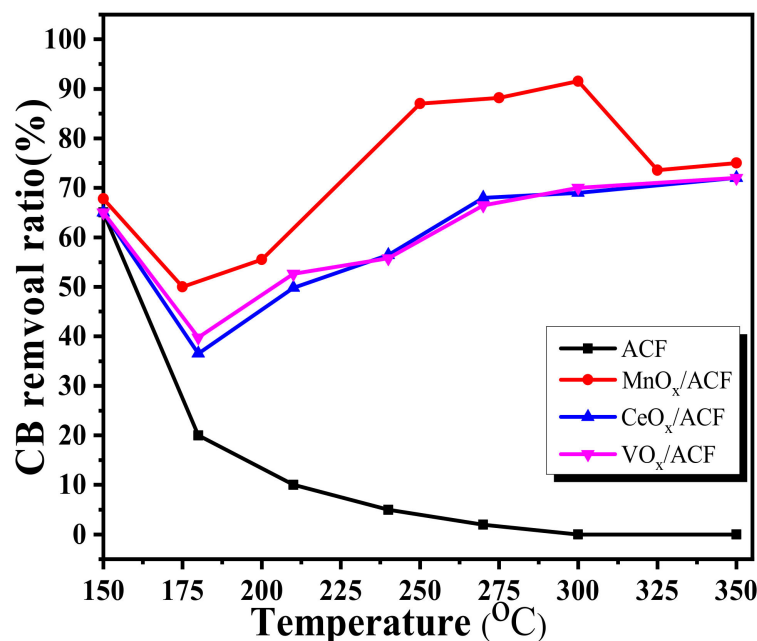


Figure 8. Adsorption/catalytic oxidation of CB over $\text{MO}_x\text{/ACF}$ with various transition metal oxides. ($C_{\text{inlet,CB}} = 5000$ ppm, Gas flow rate = 100 SCCM, GHSV = 20,000 h^{-1} , 21% O_2 , N_2 balance, dwell time = 3 h).

As described above, the CB removal ratio or conversion ratio under higher temperatures was dominantly dependent on the type of TMO; it is clear that the loaded TMO was the catalytic oxidation component in the $\text{MO}_x\text{/ACF}$. Moreover, MnO_2 was the best among the tested TMOs. In order to further check the effects of loading an amount of MnO_2 onto the ACF on the CB conversion, $\text{MnO}_2\text{/ACF}$ composites with different amounts of MnO_2 (5, 8, and 10 wt%) were prepared by the incipient wetness impregnation method, and their catalytic performance was investigated. Figure 9 displays the conversion curves of the catalytic oxidation of CB over $\text{MnO}_2\text{/ACF}$ with different loading amounts of MnO_2 as a function of temperature.

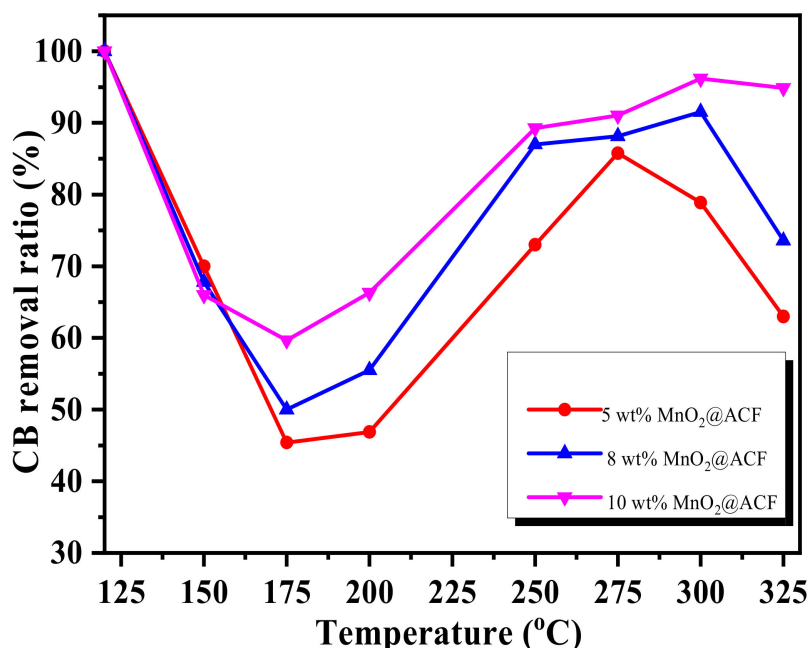


Figure 9. Adsorption/catalytic oxidation of CB over MnO₂@ACF with different amounts of manganese oxide. ($C_{inlet,CB}$ = 5000 ppm, Gas flow rate = 100 SCCM, GHSV = 20,000 h^{−1}, 21% O₂, N₂ balance, dwell time = 3 h).

As seen from Figure 9, when the bed temperature was lower than 120 °C, the CB removal ratio over all samples was almost 100% within the dwell time of 3 h; the CB removal was ascribed to the ACFs' strong adsorption capacity in this stage. Similar to the results shown in Figure 8, as the bed temperature increased, the CB removal ratio over MnO₂@ACF rose at the beginning and then declined. Surprisingly, the minimum removal ratio still reached up to 45% at 175 °C when the MnO₂ content was 5 wt%, and a higher MnO₂ content led to a higher CB removal ratio in the range of 5–10 wt%. The results demonstrated that these loaded MnO₂ nanoparticles must contribute to the high CB removal ratio at higher temperatures (>175 °C) because of their catalytic oxidation activity for CB; a higher desorption temperature for physical adsorption is in favor of the interaction between CB and MnO₂, resulting in better catalytic performance. The high efficiency of the MnO₂@ACF catalyst could be attributed to the abundant oxygen species on the MnO₂ surface [50]; the catalysis conversion of CB followed the mechanism in which chlorobenzene chemisorbed on ACF reacts with oxygen species on MnO₂ [34]. Therefore, MnO₂@ACFs is a promising dual adsorbent/catalyst for removing chlorobenzene in the full temperature range below 300 °C due to the strong adsorption capacity of ACF and the high catalytic oxidation activity of MnO₂.

4. Conclusions

In summary, a dual functional adsorbent/catalyst was successfully prepared for the high-efficiency removal of chlorine-containing volatile organic compounds (CVOCs). The ACF used the matrix acting as the catalyst carrier and adsorbent, which showed satisfying performance for loading catalysts and the adsorption of CB due to its one-dimensional fiber structure and developed porosity with a high specific surface area as well as its abundant surface functional group. TMOs were used as the catalysts and loaded onto ACF by the incipient wetness impregnation method, and three different kinds of TMOs were loaded onto ACF to produce MO_x@ACF composites.

The CB removal experiments were conducted in a fix-bed reactor, and the pristine ACF and TMOs@ACF were used to remove CB separately. The CB removal experiment results demonstrated that ACF can be used as a very efficient adsorbent for the removal of

low-concentration CB at a low temperature of 120 °C. The breakthrough time of CB over pristine ACF can reach 15 h at the inlet concentration of 5000 ppmv and space velocity of 20,000 h⁻¹, and the calculated adsorption capacity of CB over ACF at 120 °C was as high as 628.35 mg/g. Among the three kinds of TMOs, MnO₂ showed the maximal catalytic oxidation activity for CB conversion. When the bed temperature was above 175 °C, the CB removal mainly contributed to the catalytic oxidation of MnO₂; a preferable CB removal ratio was achieved at higher temperatures in the presence of more MnO₂. Therefore, CB can be effectively removed by the dual adsorbents/catalysts of MnO₂@ACF at a full temperature range below 300 °C.

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