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Enhanced removal of acetaminophen from synthetic wastewater using multi-walled carbon nanotubes (MWCNTs) chemically modified with NaOH, HNO$_3$/H$_2$SO$_4$, ozone, and/or chitosan

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Abstract
This study investigates the technical feasibility of MWCNTs for acetaminophen (Ace) removal from synthetic wastewater in batch mode. To improve their removal performance, the surface of the MWCNTs was chemically modified with NaOH, HNO$_3$/H$_2$SO$_4$, ozone and/or chitosan. The effects of pertinent parameters such as reaction time, dose, pH, and agitation speed on the Ace removal were evaluated. Their removal performance on Ace was compared to those of previous studies. The adsorption mechanisms of Ace removal by the MWCNTs are also presented. It is evident from this study that after chemical modification on its surface, the treated nano-adsorbent significantly enhanced Ace removal from wastewater. Among all types of those adsorbents, the ozone-treated MWCNT stands out for the highest Ace removal (95%) under the same initial Ace concentration of 10 mg/L. Their adsorption capacities, applicable to the Freundlich isotherm model, are listed as: ozone-treated MWCNT (250 mg/g) > chitosan-coated MWCNT (205 mg/g) > acid-treated MWCNT (160 mg/g) > NaOH-treated MWCNT (130 mg/g) > as-received MWCNT (90 mg/g). Although the ozone-treated MWCNT has the most outstanding performance in Ace removal, its treated effluent still could not meet the required effluent limit of less than 0.2 mg/L set by China’s legislation. This suggests that further treatment using biological processes needs to be carried out to complement Ace removal from the wastewater samples.

Keywords: Endocrine disruptor; Nanomaterials; Pharmaceuticals and personal care product (PPCPs); Physico-chemical Treatment; Water purification

Remarks: the first and second authors equally contributed to this article
1. Introduction

In recent years, pharmaceuticals and personal care products (PPCPs), which are not easily biodegradable and possess serious threats to public health, have been identified as one of emerging contaminants [1-2]. Compared to persistent organic pollutants (POPs) such as pesticides, pollutants from PPCPs category are distinguished by their high polarity and low volatility [3].

Among the various PPCPs, acetaminophen (Ace) has been identified as one of the most widely used drugs for fever and headache [4]. The drug is toxic when it is overdosed, as it causes acute liver and kidney failure [5]. The pollutant is often found in the municipal sewage effluents with varying concentrations from 0.1 to 10 mg/L. After conventional treatment using biological processes, the Ace, however, is still detected in sewage treatment plants and surface water [6]. Therefore, there is a growing concern regarding its implications on the aquatic environment, since biological processes alone cannot remove the pollutant effectively from contaminated water [7].

Among various physico-chemical treatments [8], adsorption may be technically feasible and cost-effective to remove this pollutant. Basically, it is a mass transfer process where a substance is transferred from a liquid phase to the surface of adsorbent and becomes bound by physico-chemical interactions [9]. Over the past years, granular activated carbon (GAC) in bulk form has been widely used to eliminate pollutants such as heavy metals [10-13]. Considering that nano-sized materials have properties different from their corresponding bulk forms, it is necessary to explore the applicability of carbon nanotubes (CNT) for Ace removal.

Due to its unique characteristics such as small size, uniform pore distribution, reactivity and large surface area per mass ratio [14], CNT represents one of the most promising functional nanomaterials for water treatment applications. It is a sheet of graphite rolled into a tubular structure, of which its building block consisting of carbon atoms [14]. Based on the hybridized carbon atom layers and diameter range, CNT is classified either as single-walled carbon nanotube (SWCNTs) or as MWCNTs. In this study, MWCNTs were tested, as their purity was higher and more cost-effective than that of the former [15].

Although the MWCNTs have been widely used for the removal of inorganic pollutants like heavy metals [16-18], to the best of our knowledge, their applications for treatment of wastewater laden with organic pollutants have been rarely reported in the literature. A preliminary study has been conducted by Tao et al. [19] on Ace removal using graphene/TiO₂ nanotubes. However, their study did not provide any information on their surface modification to improve their removal performance.
In this study, oxidative pretreatments using oxidizing agents such as nitric/sulfuric acid or ozone were used to modify the surface of the MWCNTs. This method could attach oxygenated complexes such as carboxyl, lactone, phenol, and ketone on their surface [20-22] and increase their surface charge density, making them become more hydrophilic to attract adsorbate in aqueous solutions through columbic forces [23]. While oxidative pretreatment may enlarge its surface area, alkaline pretreatment of the MWCNT could increase the concentration of oxygenated complex on their surface for enhancing adsorption process [24-25].

The laboratory study reported in this article investigates the technical feasibility of MWCNTs for Ace removal from synthetic wastewater in batch modes. Due to its potential adsorbability on MWCNT, Ace was used as a model compound of PPCPs. To improve its removal performance, the surface of MWCNT was chemically modified with NaOH, HNO$_3$/H$_2$SO$_4$, chitosan and/or ozone. The effects of parameters such as contact time, dose, pH, and agitation speed on Ace removal were evaluated. Their Ace removal performance is compared to those of previous studies. The adsorption mechanisms of Ace removal by the MWCNT are also presented.

2. Materials and Methods

2.1 Materials

With their outer diameters of 8 nm, lengths of about 10 nm, and purity of 98%, the MWCNT samples were supplied by Chengdu Chemicals (Chengdu, China). Other chemicals such as NaOH, HNO$_3$, H$_2$SO$_4$, obtained from Sigma Aldrich (China), were of analytical grade. Acetaminophen, provided by Acros (New Jersey, USA), was used as a source of synthetic wastewater. Its characteristics are presented in Table 1. The pH of Ace solution, adjusted by 0.1 M NaOH or 0.1 M H$_2$SO$_4$, was measured using a pHmeter (model Mettler FE 20, Switzerland). All of the standard solutions were freshly prepared from a stock solution using deionized water.

<table>
<thead>
<tr>
<th>Properties of acetaminophen.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Molecular formula</strong></td>
</tr>
<tr>
<td>Acetaminophen</td>
</tr>
</tbody>
</table>

Source: [19]
2.2 Surface modification of MWCNT samples

2.2.1 Alkali pretreatment of MWCNT with NaOH

To remove any remaining impurities during their production, the MWCNT samples were repeatedly washed with deionized water. Afterwards, they were soaked in 0.1 M NaOH solution with a volume ratio of 1:7 for 24 h at 150 rpm of agitation speed. The same samples were then thoroughly washed with deionized water until their solution pH became neutral. Subsequently, the samples were dried in an oven overnight at 100°C and stored in a desiccator. The samples were referred as ‘NaOH-treated MWCNT’.

2.2.2 Oxidation of MWCNT with HNO₃/H₂SO₄

About 10 g of MWCNT samples were immersed in a mixture of 0.1 M HNO₃/H₂SO₄ solution with a volume ratio of 1:3. After undergoing ultrasonic treatment for 4 h at 60°C, they were cooled and their supernatants were drained. The samples were repeatedly washed with deionized water until their solution pH was stable. Finally, the samples were dried in an oven for 24 h at 100°C and stored in a desiccator for further studies. They were labeled as ‘acid-treated MWCNT’.

2.2.3 Coating MWCNT with chitosan

Approximately 10 g of chitosan flakes (90% deacetylated) were immersed with 0.1 L of 1% (v/v) CH₃COOH and mechanically agitated using a rotary shaker at 150 rpm for 24 h to form a homogenized gel. Then, about 0.1 g of the sample (after oxidation with HNO₃/H₂SO₄) was dipped into 0.5 L of chitosan-acetic acid solution and the suspension was magnetically stirred for 24 h. Afterwards, the gel-coated MWCNTs was repeatedly washed with 1% (v/v) CH₃COOH to remove any remaining chitosan in the solution. They were dried in an oven overnight and labeled as ‘chitosan-coated MWCNT’.

2.2.4 Ozonation of MWCNT

Ozonation of the samples was carried out by an ozone generator (model WH-X-10, Nanjing, China) using ambient air as the feeding gas. In a closed system, the samples were continuously treated with gaseous ozone at an inflow concentration of 6 mg/L and a flow rate of 1.8 L/min (a mass rate of 10.8 mg/min) for 12 h. After ozonation, the samples were thoroughly washed with deionized water and dried in an oven overnight at 100°C. The samples were called as ‘ozone-treated MWCNT’.
2.3 Characterization of MWCNT

To detect changes in their morphologies before and after pretreatment, characterization methods were employed. Firstly, their morphologies were analyzed using a scanning electron microscope (SEM) model Zeiss Sigma (Germany), which operated at 15 kV. Fourier transform infrared (FTIR) spectroscopic measurements (model IS50 Thermo, USA) were also undertaken to identify certain vibrations of chemical bond in the samples. Their chemical structures were analyzed using an X-ray power diffraction (XRD) model Rigaku Ultima IV (Japan), which operated at 40 KV and 30 mA. A range of diffraction angles (2θ) from 10° to 80° at a scanning speed of 10°/min were applied.

2.4 Batch adsorption experiments

Batch experiments were conducted at ambient temperature under optimized dose, pH, agitation speed and reaction time. Subsequent tests were undertaken with only optimized parameters. After attaining equilibrium, the samples were periodically collected and filtered using a 0.22 μm nylon filter. All of the tests were carried out in triplicate and their relative standard errors were less than 5%. When the relative error exceeded this criterion, the data were disregarded and the forth experiment would be conducted until the relative error fell within an acceptable range.

2.5 Regeneration of MWCNT

Before undertaking regeneration experiments, the spent MWCNTs were separated from synthetic wastewater by filtration. The samples were then thoroughly washed with deionized water and ultrasonically treated for 10 mins. Afterwards, the same samples were dried at 100°C for 8 h and grinded again. The spent MWCNTs were then regenerated and reused for Ace removal.

2.6 Chemical analysis

The remaining Ace concentration after treatment was analyzed using a spectrophotometer (model Mapada UV1800, Shanghai, China) at its maximum wavelength (λ) of 243 nm. The amount of Ace adsorbed by the MWCNT was calculated using the Equations (1) and (2), respectively:

\[ q_e = \frac{c_0 - c_e}{w} \]  
\[ \eta(\%) = \left(\frac{c_0 - c_1}{c_0}\right) \times 100\% \]

where \( q_e \) is the amount of Ace adsorbed by the adsorbent at equilibrium (mg/g), while \( c_0 \) (mg/L)
and $C_e$ (mg/L) are the initial and the equilibrium concentrations, respectively; the $C_t$ (mg/L) is the Ace concentration in liquid phase at any given time $t$ (min), while $W$ and $\eta$ are the weight of the samples in the solution (g/L) and the removal efficiency (%) of Ace after treatment, respectively.

3. Results and Discussion

3.1 MWCNT characterization

3.1.1 FTIR spectra analysis

![FTIR spectra of MWCNTs](image)

Fig. 1. The FTIR spectra of the MWCNTs before and after pretreatment.

The FT-IR spectra, depicted in Fig. 1, were used to identify the chemical bonds and/or functional groups present on the MWCNTs after their surface modifications. It is obvious that new bands were present for the chemically treated MWCNTs, as compared to their as-received form. The peak around 3430 cm$^{-1}$ was related to the -OH group, resulting from acidic pretreatment and/or ozonation on the surface of the MWCNT, while the peak at 1630 cm$^{-1}$ could be an indicative of the stretching vibration of the C=O from the –COOH group. This particular peak was related to the acid-treated MWCNT and/or the chitosan-coated MWCNT.

Another broad peak at 1000 cm$^{-1}$ for the acid-treated MWCNT was also related to the stretching of C-O bonds. This increment of oxygenated surface groups implies the presence of carboxylic groups on the samples after oxidative pretreatment.
3.1.2. X-ray diffraction (XRD) analysis

![X-ray diffraction patterns of all the obtained MWCNTs.](image)

Fig. 2. X-ray diffraction patterns of all the obtained MWCNTs.

To identify changes in the structure of the samples from amorphous to crystalline after surface modification with strong oxidizing agents, X-ray diffraction tests were employed to determine their crystalline structures. The XRD results, presented in Fig. 2, indicate that various pretreatments of the samples did not change the original peaks of the as-received MWCNT. This suggests that the chemical modification on their surfaces did not damage the adsorbents’ crystal structures.

3.1.3. SEM analysis

SEM analyses were also employed to detect changes in the morphology of the MWCNTs. Fig. 3 presents SEM images of all chemically treated MWCNTs.
Fig. 3. SEM of (a) as-received MWCNT, (b) NaOH-treated MWCNT, (c) HNO₃/H₂SO₄-treated MWCNT, (d) chitosan-coated MWCNT, (e) ozone-treated MWCNT.

It is obvious from Fig. 3b that pretreatment with NaOH changed its morphology and pore characteristics. Pores of different size and shape could be observed from the tiny holes present in the NaOH-treated MWCNT, while the morphology of the ozone-treated MWCNTs presents an enhanced dispersion due to the presence of –COO group on their surface. This could be explained due to the fact that their ozonation promoted Ace adsorption by (i) increasing the concentration of oxygenated surface complex; (ii) improving the quantity of acidic surface oxygen functional groups such as carboxylic, carbonyl, and phenol [26]; (iii) enhancing the textural features of the adsorbent [27]; and (iv) changing the acid/base characteristics of the nanomaterial [28].

As depicted in the Fig. 3d, the chitosan particles not only attach to the surface of the MWCNT, but also fill into the interspace of the tubes. This finding confirms those of the study undertaken by Castrejón-Parga et al. [29], who demonstrated that the chitosan particles were wrapped on the surface of MWCNTs after their pretreatment. The SEM image of the ozone-treated MWCNTs (Fig 3e) indicates their aggregation and surface roughness. Their outer walls appeared to be smoother and more even than those of the as-received MWCNTs [30].
3.2 Adsorption studies

3.2.1 Effects of contact time

Since equilibrium time is an important parameter for a cost-effective water treatment, it is necessary to determine optimum contact time in Ace removal by the modified MWCNTs. The Ace removal, studied as a function of contact time in Fig. 4, was undertaken at 10 mg/L of Ace initial concentration with 1 g/L of adsorbents.

![Graph showing Ace removal efficiency as a function of contact time for different types of MWCNTs.](image)

**Fig. 4.** Effects of contact time on Ace removal by all types of MWCNT (10 mg/L of Ace; 1.0 g/L of adsorbents; 170 rpm; 25°C).

Fig. 4 shows that the Ace removal efficiency improved with an increasing contact time and it tended to level after equilibrium, a point where there is a defined distribution of adsorbate between solid and liquid phases. In the first 40 min, the Ace removal by the acid-treated MWCNT, the chitosan-coated MWCNT and the ozone-treated MWCNT significantly increased and attained the equilibrium within 1 h. Among the various types of MWCNTs, the ozone-treated MWCNT has the highest Ace removal (88%) at the same Ace concentration of 10 mg/L.

It was found that there was a substantial difference in terms of Ace removal efficiency between the as-received MWCNT and the chemically modified MWCNTs. This could be due to the fact that the optimum contact time was affected by the ratio of the number of free adsorption sites to the number of Ace molecules. After surface modification, the number of available adsorption sites of the chemically treated MWCNTs was significantly enhanced. As a result, the Ace removal proceeded rapidly, as more Ace species were adsorbed onto their surfaces.
Overall, the contact time required by the chemically modified MWCNTs was relatively short. One hour of contact time was selected for the remaining adsorption studies.

3.2.2 Effects of dose

Since dose of adsorbent reflects the number of free adsorption sites for adsorbates, their effects on Ace removal by the MWCNT was investigated by varying their dose from 0.05 to 3 g/L, while keeping other parameters (C₀, pH and agitation speed) remained constant.

![Graph showing the effects of adsorbents dosage on the removal of Ace by all types of MWCNTs](image)

**Fig. 5.** Effects of adsorbents dosage on the removal of Ace by all types of MWCNTs (10 mg/L of Ace; 170 rpm; 25°C).

Fig. 5 demonstrates that the Ace removal by the adsorbents improved with an increasing dose up to a certain value and then there was no further Ace removal. At the same Ace concentration of 10 mg/L, the Ace removal was significantly enhanced from 25% to 87% when the dose of the ozone-treated MWCNT increased from 0.1 to 1.0 g/L (Fig. 5). This stems from the fact that the higher the dose of the adsorbent, the greater the availability of exchangeable sites for Ace molecules [31].

It was also found that their adsorption capacities of the chemically treated MWCNT varied due to different types of pretreatment. The ozone-treated MWCNT has the highest Ace removal, as the ozonation pretreatment of the samples might have changed their chemical structures due to the presence of additional functional groups like hydroxyl and carboxyl on their surface.

Although the ozone-treated MWCNT had the most outstanding Ace removal, their treated effluents still could not meet the required Ace effluent limit of less than 0.2 mg/L set by China’s legislation [32]. This suggests that further biological process is required to complete Ace removal.

10 / 27
from the wastewater samples.

3.2.3 Effects of pH

Solution pH in adsorption is important, as it affects not only the physico-chemical properties of adsorbate, but also the surface charge of adsorbent [33]. This parameter plays roles in promoting electrostatic interactions between the adsorbate and the adsorbent during the treatment [34]. To understand its effects on Ace adsorption, pH was varied from 2 to 10.

**Fig. 6.** Effects of pH on Ace removal by all types of MWCNTs (10 mg/L of Ace; 170 rpm; 25°C; dose: optimum).

Fig. 6 shows that the Ace removal efficiency of the MWCNT improved when their pH varied from 2 to 4 and then decreased over the pH range from 4 to 10. This could be due to the fact that a lower pH increased the negatively charged groups on their surface, leading to a higher Ace removal.

The surface properties of the adsorbents play roles in Ace removal, while solution pH affects the dissociation of functional groups on their surface. After its pretreatment with ozone, the surfaces of the MWCNT, a π electron-rich region [34-35], introduced additional carboxylic and hydroxyl groups, as indicated by Fig. 1. As depicted by Fig 6, at pH 4 and 5, more Ace species were adsorbed onto the surface of the ozone-treated MWCNTs through attractive columbic forces, leading to a maximum removal of the adsorbate [36].

3.2.4 Effects of agitation speed

Effects of agitation speed on Ace removal were studied by varying it from 90 to 190 rpm, while
keeping dose and pH constant. Fig. 7 illustrates the effects of agitation speed on Ace removal by all types of MWCNTs.

![Fig 7](image_url)

**Fig 7.** Effects of agitation speed on Ace removal by all types of MWCNTs (10 mg/L of Ace; 25°C; dose and pH: optimum).

Fig. 7 shows that the Ace removal by all types of MWCNTs slightly improved with the increasing agitation speed. The Ace removal by the ozone-treated MWCNT was enhanced from 73% to 95% when the agitation speed increased from 90 to 190 rpm. This could be attributed to the fact that increasing agitation speed decreased the resistance of the boundary layer for mass transfer by the adsorbent, leading to a higher driving force for Ace removal [37]. In addition, a higher agitation speed increased the intensity of physico-chemical interactions between the negatively charged surface of the adsorbent and the positively charged Ace at acidic conditions.

Overall, this parameter did not affect the extent of Ace removal by the MWCNT. The agitation speed of 190 rpm was selected for the remaining studies.

### 3.3 Adsorption kinetic

Adsorption kinetics is important, as it describes the rate of adsorbate uptake. The kinetic parameters provide information for modeling the adsorption processes [38]. In this study, both pseudo-first order and second-order kinetic models were employed to simulate the experimental data by varying the dose of the adsorbent.

The pseudo-first-order model was used to describe the experimental data based on the following
equation [39]:

\[ \ln(q_e - q_t) = \ln(q_e) - k_1 t \]  \hspace{1cm} (3)

where \( q_e \) and \( q_t \) are the amount of Ace adsorbed at equilibrium (mg/g) and at time \( t \) (min) respectively. The value of \( k_1 \) (min\(^{-1}\)), calculated from the plots of \( t \) against \( q_t \) for different obtained MWCNTs, is the pseudo-first order kinetic constant. Both \( q_e \) and \( k_1 \) are calculated from the intercept and the slope of the kinetic plot of \( t \) against \( q_t \) respectively.

Fig. 8a shows that the kinetic rate of the ozone-treated MWCNT was higher during the initial stage of adsorption than those of other modified MWCNTs, suggesting that the adsorbent achieved the equilibrium earlier than the others. Among all types of MWCNTs, the as-received MWCNT had the lowest kinetic rate.

\[ \frac{t}{q_t} = \frac{1}{(q_e^2 k_2)} + \frac{t}{q_e} \]  \hspace{1cm} (4)

where \( q_t \) and \( q_e \) represent the amount of Ace adsorbed at time \( t \) (min) and at equilibrium respectively. The amount adsorbed \( q_e \) (mg/g) and the pseudo-second order rate constant \( k_2 \) (min\(^{-1}\))
are obtained from the intercept and the slope of the kinetic plot of $t$ against $q_t$ respectively. As presented in Table 2, the correlation coefficients of the pseudo-second-order model are higher than 0.98, suggesting that the second-order kinetic model was more representative than the first-order kinetic model.
Table 2

Kinetic parameters of Ace adsorption by all types of MWCNTs.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>As-received MWCNT</th>
<th>NaOH-treated MWCNT</th>
<th>HNO₃/H₂SO₄-treated MWCNT</th>
<th>Chitosan-coated MWCNT</th>
<th>Ozone-treated MWCNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>$q_e$ (mg/g)</td>
<td>4.70</td>
<td>5.66</td>
<td>8.63</td>
<td>8.68</td>
<td>9.39</td>
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<tr>
<td></td>
<td>$k_1$ (min⁻¹)</td>
<td>0.025</td>
<td>0.040</td>
<td>0.029</td>
<td>0.044</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.9875</td>
<td>0.9921</td>
<td>0.9691</td>
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<td>0.9704</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>$q_e$ (mg/g)</td>
<td>6.50</td>
<td>7.15</td>
<td>9.50</td>
<td>10.99</td>
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<td></td>
<td>$k_2$ (%·min⁻¹)</td>
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<td>$R^2$</td>
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<td>0.9986</td>
<td>0.9803</td>
<td>0.9855</td>
<td>0.9843</td>
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</table>
3.4 Adsorption isotherm

To design an adsorption system for Ace removal, it is important to establish the most appropriate correlation for equilibrium curves. Thus, equilibrium data are represented by adsorption isotherms, which correspond to the relationship between the mass of Ace adsorbed per unit mass of MWCNT \( (q_e) \) and the concentration of adsorbate in the liquid phase at equilibrium \( (C_e) \). In this study, the adsorption isotherm of Ace onto MWCNT was simulated by using both the Langmuir and the Freundlich isotherm models.

The Langmuir model assumes uniform adsorption energies onto a homogeneous surface without interaction among the adsorbate molecules on the carbon surface. The Langmuir isotherm can be expressed by the Equation (5) [41]:

\[
q_e = q_{\text{max}} \frac{bC_e}{1+bC_e}
\]  

(5)

where \( q_e \) and \( C_e \) are the amount of Ace adsorbed (mg/g) and the equilibrium concentration of the adsorbate (mg/L) respectively, while \( q_{\text{max}} \) and \( b \) are the Langmuir constants, determined from the slope and the intercept of the linear plot of \( C_e \) versus \( q_e \) (Fig. 9).

Unlike the Langmuir, the Freundlich isotherm model assumes that the uptake of adsorbate occurs on a heterogeneous surface and that the amount of the adsorbate adsorbed increases infinitely with an increasing concentration [41]. The removal of Ace by the MWCNT was studied using the Freundlich model in Equation (6):

\[
q_e = K_f C_e^{1/n}
\]  

(6)

where \( K_f \) and \( n \) are the constants of the Freundlich isotherm incorporating adsorption capacity (mg/g) and intensity, while \( C_e \) and \( q_e \) represent the remaining concentration of adsorbate at equilibrium (mg/L) and the amount of Ace adsorbed (mg/g) at equilibrium condition respectively.

When the same experimental data were plotted as \( C_e \) against \( q_e \) (Fig. 9), a plot with the slope \( \frac{1}{n} \) was obtained for all adsorbents. The \( R^2 \) values, a measure of goodness of fit for the plots, are presented in Table 3. As confirmed by their \( R^2 \) values, the Freundlich isotherm model was more representative for all types of the MWCNTs than the Langmuir model, indicating that multilayer
adsorption occurred on their surface. The $n$ values of the modified MWCNT, ranging from 2 to 3, suggest a heterogeneous adsorption of Ace during the treatment [17].

![Graph showing adsorption isotherms for different types of MWCNT](image)

**Fig 9.** (a) Langmuir model; (b) Freundlich model for Ace adsorption by MWCNT.

Table 3 shows that the ozone-treated MWCNT have the highest Ace adsorption capacity, as compared to the others. One possible reason is that pretreatment by ozonation introduced additional basic oxygen-containing functional groups, which have a higher affinity to Ace, on its surface [42]. The oxygen-containing surface groups formed during ozonation are basic pyrone-type groups, which contain two non-neighboring oxygen atoms, constituting one basic site. The basic groups are the Lewis type associated with $\pi$ electron-rich regions found within the basal plane [43-45].
Table 3
Parameters of the Langmuir and Freundlich isotherm model for Ace removal by all types of MWCNTs.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
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<th>Chitosan-coated MWCNT</th>
<th>Ozone-treated MWCNT</th>
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<tbody>
<tr>
<td>Langmuir model</td>
<td>$b$ (L/mg)</td>
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<td>2.80</td>
<td>3.05</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9842</td>
<td>0.9813</td>
<td>0.9864</td>
<td>0.9937</td>
<td>0.9788</td>
</tr>
</tbody>
</table>
3.5 Adsorption mechanism of MWCNT

Some studies provided information on the Ace removal by carbonaceous materials due to their basic oxygen-containing surface functional groups [26]. The mechanisms, which contribute to its adsorption, include: (i) electrostatic interactions; (ii) electron donor-acceptor complex formation due to π-π dispersive forces between the basic surface carbonyl group and the aromatic ring of the adsorbate; and (iii) H-bonds between the surface carbonyl group and the OH group of the Ace. Such mechanisms could be applicable [46-47], depending on the adsorbent’s surface chemistry that plays key roles during the Ace removal [34].

Among the adsorption mechanisms listed above, dispersive π-π interaction mechanism is the most reasonable in this study. One possible reason is the attractive interactions of the two π-electron orbitals between the electronic density in the adsorbate’s aromatic ring and the adsorbent’s basal plane through electron donor-acceptor mechanisms [48]. Each aromatic ring of the adsorbent has a π-electron orbital below and above the plane of six atom carbon. When the Ace molecules are adsorbed on the adsorbent, their aromatic π-electrons directly interact with the π-electrons of the aromatic ring of the MWCNT.

The Ace adsorption by the adsorbent is enhanced when more π-electrons are present on its basal planes that act as the Lewis basic group by donating delocalized π-electron pairs. The dispersive interactions between the π-electrons of the aromatic ring of the adsorbate acting as acceptor and those of the surface carbonyl group in the graphenic layer of the adsorbent result in the formation of electron donor-acceptor complexes that control the Ace removal. The complexes improve the capacity of the aromatic ring of Ace to accept the π-electrons donated by the functional groups of the surface to form chemical interactions [49].

3.6 Regeneration studies

Regeneration of adsorbent that enables it to maintain adsorption capacity for subsequent use is critical for cost-effective wastewater treatment applications. The regeneration efficiencies of the spent MWCNT are presented in Table 4. During regeneration, the Ace removal by all types of the spent MWCNTs decreased from one cycle to another. These findings are in agreement with those reported by Shan et al. [50], who used regenerated granular carbon nanotubes for removal of various pharmaceuticals from wastewater.
Table 4
Regeneration efficiencies of spent MWCNTs on Ace removal rate (10 mg/L of Ace, dose, pH, agitation speed: optimum).

<table>
<thead>
<tr>
<th>Removal rate (%)</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
<th>Cycle 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received MWCNT</td>
<td>46</td>
<td>32</td>
<td>27</td>
<td>25</td>
</tr>
<tr>
<td>NaOH-treated MWCNT</td>
<td>66</td>
<td>51</td>
<td>42</td>
<td>38</td>
</tr>
<tr>
<td>HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4}-treated MWCNT</td>
<td>84</td>
<td>72</td>
<td>63</td>
<td>59</td>
</tr>
<tr>
<td>Chitosan-coated MWCNT</td>
<td>93</td>
<td>73</td>
<td>59</td>
<td>47</td>
</tr>
<tr>
<td>Ozone-treated MWCNT</td>
<td>95</td>
<td>80</td>
<td>71</td>
<td>65</td>
</tr>
</tbody>
</table>

3.7 Comparison of Ace removal in this studies and previous studies

To justify their technical feasibilities as effective adsorbents for removal of organic pollutants, the adsorption capacities of modified MWCNTs in this study were compared with those of other adsorbents. Table 5 presents a summary of various adsorbents for organic pollutants’ removal. To compare their viability, comparative studies are made with respect to adsorption capacity (mg/g), optimum pH, agitation speed (rpm) and temperature (K). This comparison has a relative meaning due to different testing conditions (pH, temperature, and wastewater composition), types of adsorbent and chemical modification.

Various materials have been used for removal of organic pollutants from wastewater such as activated carbon, CNT, and fly ash. It is clear from Table 5 that after oxidation, the adsorption capacities of those adsorbents were enhanced. Sulfuric acid-treated activated carbon was reported to be effective for Ace removal with an adsorption capacity of 900 mg/g [51]. An adsorption capacity of 110 mg/g for lincomycin (LCN) was reported by Kim et al. [56] for the SWCNT. Treated MWCNTs with HNO\textsubscript{3} [40], or NaClO [36], or carboxylation [37] were also effective for the removal of Cu (II) (108 mg/g), ciprofloxacin (175 mg/g) and linear alkyl benzene sulfonates (160 mg/g) respectively.

In this study, different types of treated MWCNTs were tested to remove Ace from synthetic wastewater. The ozone-treated MWCNT has the highest Ace adsorption capacity (250 mg/g) under the same optimum conditions, as compared to others. In spite of its promising results, further investigations are still required to improve its regeneration efficiencies.
Table 5
Summary of adsorption capacities by various adsorbents for organic pollutants.

<table>
<thead>
<tr>
<th>Type of adsorbent</th>
<th>Dose of adsorbent (g/L)</th>
<th>Type of pollutant</th>
<th>Concentration of pollutant (mg/L)</th>
<th>Optimum pH</th>
<th>Time (min)</th>
<th>T (K)</th>
<th>Removal efficiency (%)</th>
<th>Q_{\text{max}} (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone-treated MWCNT</td>
<td>1</td>
<td>Ace</td>
<td>1000</td>
<td>4</td>
<td>60</td>
<td>298</td>
<td>95</td>
<td>250</td>
<td>Present study</td>
</tr>
<tr>
<td>^aACP</td>
<td>2</td>
<td>Ace</td>
<td>105</td>
<td>7</td>
<td>3000</td>
<td>298</td>
<td>NA</td>
<td>52</td>
<td>[53]</td>
</tr>
<tr>
<td>fly ash</td>
<td>0.24</td>
<td>Ace</td>
<td>400</td>
<td>NA</td>
<td>60</td>
<td>303</td>
<td>60</td>
<td>200</td>
<td>[54]</td>
</tr>
<tr>
<td>^bDGO</td>
<td>0.02</td>
<td>Ace</td>
<td>100</td>
<td>8</td>
<td>120</td>
<td>298</td>
<td>19</td>
<td>704</td>
<td>[52]</td>
</tr>
<tr>
<td>^c-f-GC</td>
<td>0.05</td>
<td>Ace</td>
<td>480</td>
<td>5</td>
<td>300</td>
<td>303</td>
<td>90</td>
<td>270</td>
<td>[55]</td>
</tr>
<tr>
<td>H_{2}SO_{4} treated ^dAC</td>
<td>4.33</td>
<td>Ace</td>
<td>750</td>
<td>7</td>
<td>NA</td>
<td>300</td>
<td>NA</td>
<td>900</td>
<td>[51]</td>
</tr>
<tr>
<td>SWCNT</td>
<td>NA</td>
<td>^f-LCN</td>
<td>NA</td>
<td>NA</td>
<td>360</td>
<td>293</td>
<td>90</td>
<td>110</td>
<td>[56]</td>
</tr>
<tr>
<td>AC</td>
<td>1</td>
<td>^g-ATE</td>
<td>250</td>
<td>7</td>
<td>240</td>
<td>298</td>
<td>43</td>
<td>144</td>
<td>[57]</td>
</tr>
<tr>
<td>HNO_{3}-treated MWCNT</td>
<td>0.1</td>
<td>Cu (II)</td>
<td>60</td>
<td>3</td>
<td>60</td>
<td>298</td>
<td>82</td>
<td>108</td>
<td>[40]</td>
</tr>
<tr>
<td>NaClO-treated MWCNT</td>
<td>0.5</td>
<td>^h-CPX</td>
<td>150</td>
<td>4</td>
<td>240</td>
<td>298</td>
<td>42</td>
<td>175</td>
<td>[36]</td>
</tr>
<tr>
<td>^e-CMMWCNT</td>
<td>0.01</td>
<td>^i-LAS</td>
<td>50</td>
<td>5</td>
<td>120</td>
<td>298</td>
<td>97</td>
<td>160</td>
<td>[37]</td>
</tr>
</tbody>
</table>

Remarks:
^aACP: activated carbon pellets;
^bDGO: double-oxidized graphene oxide;
^c-f-GC: gasification chars mixed with ground K_{2}CO_{3};
^dAC: activated carbon;
^e-CMMWCNT: carboxyl modified multi-walled carbon nanotubes;
^f-LCN: lincomycine;
^h-CPX: ciprofloxacin;
^i-LAS: linear alkylbenzene sulfonates
4. Conclusions

This study has demonstrated the technical applicability of the modified MWCNTs for the removal of Ace from contaminated water. After chemical modification on its surface, it was evident that the treated nano-adsorbents significantly enhanced Ace removal from synthetic wastewater. Among those adsorbents, the ozone-treated MWCNT stands out for the highest Ace removal (95%) under the same initial Ace concentration of 10 mg/L. Their adsorption capacities, applicable to the Freundlich isotherm model, are listed as follows: ozone-treated MWCNT (250 mg/g) > chitosan-coated MWCNT (205 mg/g) > acid-treated MWCNT (160 mg/g) > NaOH-treated MWCNT (130 mg/g) > as-received MWCNT (90 mg/g). Although the ozone-treated MWCNT has the most outstanding performance in Ace removal, its treated effluent still could not meet the required effluent limit of less than 0.2 mg/L set by China’s legislation. This suggests that further treatment using biological process needs to be carried out to complement Ace removal from the wastewater samples.

Acknowledgements
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References:


Graphical abstract

SEM analyses of (a) as-received MWCNT, (b) NaOH-treated MWCNT, (c) HNO$_3$/H$_2$SO$_4$-treated MWCNT, (d) chitosan-coated MWCNT, (e) ozone-treated MWCNT.
Highlights

- Ace removal by MWCNT after surface modification with O₃ was significantly enhanced.
- Ozone-treated MWCNT has the highest Ace adsorption capacity under the same conditions.
- The adsorption isotherms of all MWCNTs are applicable to the Freundlich model.