A Review in Tetracycline Removal from Water Environment by Carbon Nanotubes Adsorption

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Abstract. Owing to the unique properties, carbon nanotubes (CNTs) have been widely reported as a desirable adsorbent for environmental pollutants removal. In this paper, the synthetic strategies of different kinds of CNTs and CNTs based composites, as well as their application in tetracycline antibiotics (TCs) removal were discussed. The adsorption process, performance, influence factors involved in the adsorption of tetracycline (TC) are highlighted in this review. In addition, the adsorption mechanism and limitations in adsorption TCs with CNTs are discussed.

1. Introduction
Rapid development of industries results in environmental problems[1]. TCs are kinds of widely used antibiotics which can inhibit most of pathogens, viruses and protozoans [2]. However, the abuse of TCs makes TC entering water environment through microbes, medical drugs, agricultural drugs, and sewage treatment plants, which causes high level residual of them in water environment. Thus, it is essential to remove TCs in water environment. Nowadays, the removal methods of TC in the environment mainly include biodegradation, electrochemical oxidation, fenton reaction and adsorption. Adsorption is the physical adherence or bonding of ions and molecules onto the surface of another molecule [3]. But they usually need large area and long reaction time, and may produce toxic by-products. As a new adsorbent, CNTs, have attract increasing attention of researchers [4] and have been widely used in environmental pollution control [5].

In this paper, the application of CNTs (including single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs)) and composites based on CNTs in the removal of TC antibiotics in water environment were briefly reviewed and summarized in Table 1. This study will provide guidance for researchers working in the design of CNTs and their application in antibiotic removal.

2. Adsorption of TC onto CNTs
Babaei et al. [2] reported a functionalized multi-walled carbon nanotube (MWCNT) to remove TC from aqueous solutions. It was observed the adsorption percentage of TC remained high between pH=5 and pH=7 and decreased with the pH ≤ 3 or PH > 7. Moreover, with the increase of the MWCNT dosage, both adsorbent surface area and adsorption sites also increase which result the increase of the percentage of TC removal. Further experiment indicated that only Fe\(^{3+}\) has significant effect for the adsorption of TC, which attributed to the electrostatic interaction between Fe\(^{3+}\) and MWCNT with negative charge. The adsorption of TC followed the fractionary-order kinetic, and the adsorption of TC onto the MWCNT can reach to equilibrium in 120 min. The adsorption isotherms data showed that the maximum adsorption capacity is 253.38 mg/ g. 

Zhang et al. [6] studied the optimal conditions for the absorption of TC from aqueous solution by MWCNTs. The adsorption percentage of TC can reach high percentage at PH=4.5 and remained in the
range of 4.5-7.0 (Figure 1). High adsorption percentage of TC ascribed to the non-electrostatic π-π dispersion interaction between MWCNT and TC molecules. Further studies found that ionic strength barely affected the adsorption of TC and with the amount of MWCNT exceeded 8.0 mg in 25 mL TC solutions (50 mg/L), the adsorption percentage of TC can reach 99.8%. The adsorption process can reach to equilibrium within 20 min followed the pseudo-second-order model, and can be affected by intraparticle diffusion and boundary layer diffusion. The experimental data fix the Langmuir model and the maximum adsorption capacity can reach 269.54 mg/g. In addition, desorption experiment was conducted, and more that 80% desorption percentage can be obtained with 10.0 mL 3 mol/L AlCl3 added.

**Figure 1.** Adsorption of TC with MWCNT under different pH (8.0 mg MWCNT; Temp. 20 ± 0.1 °C). [6]

Alvareztorrellas et al. [7] studied the adsorption of TC with MWCNTs and compared that with other carbonaceous materials including a commercial granular activated carbon (AC-F400), and two activated carbons (AC-PS (peach stones), AC-RH (rice husk)) prepared in laboratory. The kinetic experimental data match the pseudo-second order equation, and the adsorption capacity of AC-PS toward tetracycline can reach 845.9 mg/g which was determined by the surface chemical and textural properties of adsorbents. The C=O stretching vibrations in ketone and alkane/alkene groups played vital roles in the TC adsorption process.

Ji et al. [8] studied the mechanisms for adsorption of TC to single-walled carbon nanotubes(SWNT) and MWNT, and made a comparison with pulverized activated carbon (AC) and nonporous graphite. Adsorption isotherms with above four adsorbents towards TC fit the Freundlich sorption model, and SWNT, MWNT have higher adsorption affinity than other two materials. The study of adsorption mechanisms found that strong interactions between the graphene surface and TC caused the efficient adsorption of TC. The interactions mainly include followings (1) van der Waals forces; (2) π-π EDA interaction between the conjugated graphene π-electrons and the π-electron moieties ; (3) cation-π bonding between the graphene π-electrons and the protonated amino group. Through the solution-phase spectroscopic studies, it is found that specific molecular-level interactions between TC and carbon nanotubes can improve the adsorption selectivity and efficiency.

Ji et al. [9] investigated the adsorption of TC on carbon nanotubes with the effect of aqueous solution chemistry. With the presence of the dissolved soil humic acids (DSHA) or dissolved coal humic acids (DCHA), the adsorption of TC with MWNT was decreased 50%, whereas the adsorption of TC with SWNT was not influenced. Moreover, the adsorption of TC on MWNT was increased distinctly with the appearance of Cu²⁺ ion. Further studies showed that the addition of cation can shield the electron on negatively charged surface sites, which caused the adsorption of TC on both MWNT and SWNT was decreased with the increased of ionic strength.

Yu and co-workers [10] also explored the effects of surface properties and aqueous solution chemistry on the adsorption of TC with MWCNTs. In the experiment, the CNTs-3.2%O had the highest absorbability which can reach 269.25 mg/g. The study of adsorption kinetics found that the experimental data were best fitted to the pseudo-second-order model, and the rate in the adsorption process is influenced by both intra-particle and boundary layer diffusion. In the pH range 3.3 to 8.0,
The zwitterionic form of the TC molecule contributed the CNTs-3.2%O to have the maximum adsorption capacity and the highest removal ratio. The mechanisms of the adsorption of TC from aqueous solutions onto MWCNTs are electrostatic interactions, π-π interactions and double bonds, or hydrophobic interactions. The presence of Cu²⁺ increased the TC adsorption capacity owing to the cation bridging between the metal ion, TC and the adsorbent ligand groups.

Wang et al. [11] investigated the adsorption of TC in the aqueous solution with graphitized multi-walled carbon nanotubes (G-MWCNTs) and MWCNTs with functional groups. G-MWCNTs has the highest adsorption affinities among OH-MWCNTs, COOH-MWCNTs and NH₂-MWCNTs. Both of the adsorption data with the absence and presence of Cu(II) or Ni(II) were fitted to the Freundlich sorption model. The adsorption of TC with G-MWCNTs was not influenced by the presence of Cu(II) and Ni(II), but can improve or reduce the removal rate of TC with other MWCNTs with functional groups.

3. Adsorption of TC onto CNTs based composites
To remove TCS, i.e., TCN, OTC and CTC from aqueous solutions, Xiong et al. [12] loaded a MWCNT on an iron metal-organic framework (MIL-53(Fe)) to form a new adsorbent. From the result of MWCNT/MIL-53(Fe) SEM images (Figure 2), MIL-53(Fe) remained the original morphology and MWCNT was attached on the surface of it. The adsorption kinetics fitted to the pseudo-second-order equation, simultaneously, the adsorption isotherms fitted to the via Langmuir equations. The adsorption amount of TCs decreased with the pH values increased because of the electrostatic repulsion, and also decreased with the increase of the Na⁺ concentration because of the competitive adsorption. The maximum adsorption capacity of MWCNT/MIL-53(Fe) toward TCN, OTC and CTC can reach to 82.35, 53.79 and 38.46 mg/g respectively, which are larger than that of MWCNT and MIL-53(Fe). Mechanism studies showed that this adsorption process was ascribed to the dispersive π-π adsorbate-adsorbent interactions and TCS dimensions. Further studies showed that the stability of MIL-53(Fe) was enhanced after MWCNT modified in aqueous solutions.

Figure 2. SEM images of (a) MIL-53(Fe), (b) MWCNT, (c)MWCNT/MIL-53(Fe)-20% [12]

Balarak et al. [13] used the alumina-coated multi walled carbon nanotubes (Al₂O₃/MWCNT) to absorb TC from aqueous solution. The removal rate of TC by Al₂O₃/MWCNTs was increased rapidly in the initial 30 min, then reached a plain in 60 min with slow rate. Moreover, with the increasing of Al₂O₃/MWCNT dosage, the adsorption percentage of TC increased owing to more adsorption sites and higher surface area. The pseudo-second-order model and Langmuir isotherm model fit the data of adsorption and the maximum adsorption capacity of TC can reach 99.4 mg/g.

Zheng et al.[4] fabricated the TiO₂@MWCNTS composite adsorbents with electrostatic assembly to absorb the TC-HCl. The highest adsorption capacity was obtained when the pH reached 6. The adsorption velocity and the capacity increased with the increase of the TC-HCl concentration, and reached the highest velocity in the first 40 min. Moreover, with the increase of the dosages of TiO₂@MWCNTS, the removal rate of TC-HCL and the adsorption captivity increased and the highest unit adsorption capacity and removal rate can be obtained with 0.50 g/L TiO₂@MWCNTS. The data of adsorption was fit by the pseudo-second-order model and Langmuir isotherm model. In addition, proper addition of H₂O₂ can effectively promote the coupling of TiO₂ photocatalytic ability with H₂O₂ strong oxidation ability, thus significantly enhancing the regeneration effect.
To improve the adsorption of TC, Deng et al. [5] used oxidation and reduction process to fabricate a MWNT coated with manganese dioxide (MnO$_2$/MWNT). The Freundlich isotherm model fit the data of adsorption. TC had π-π electron interaction with the highly polarized graphene structures on the surface of MnO$_2$/MWNT (π electron donor). The increase of pH can promote the deprotonation of amino group and the protonation of enol groups, weakening the cation-π bonding, π-π EDA interaction and Lewis acid-base interaction between antibiotics and MnO$_2$/MWNT, thus causing the adsorption coefficient decreased significantly. Further studies indicated that humic acids had negligible effect on the TC adsorption with MnO$_2$/MWNT for the more competitive of TC molecule than humic acids.

4. Limitations of TC adsorption with CNTs
The structure of CNTs including oxygen-containing functional group, size of the interstice between the bundles, surface curvature and surface defects have great influence on the adsorption of TC with CNTs. Organic solvents including the molecular size and functional groups also can affect the adsorption effect. Moreover, other external factors such as ionic strength, DOM and surfactant also have an impact on the adsorption of organic pollutants.

5. Conclusions and perspectives
In this paper, it had investigated the application of CNTs for TC adsorption in aqueous solution. The adsorption capacity of TC with CNTs can be improved with composites based on CNTs fabricated or metal ion introduced in the TC aqueous solution. The main mechanism of adsorption of TC on CNTs is π-π interactions between the graphene surface and TC molecules. Kinetics, thermodynamics have been explored in most of researches. Although CNTs have the advantages of excellent adsorption capacity and high adsorption rate, they are limit in the large-scale industrialization because of high production cost. Moreover, with the increase of production and use of CNTs, their residual concentration level in the environment will increase, which may cause harm to the water environment and aquatic organisms. Hence, in the future, more research on the production cost control, regeneration of CNTs, and environmental toxicity of the CNTs will be required.

| CNTs          | Kinetic model | Isotherm model | pH     | Ion impact | qe (mg/g) | Mechanism                                      | Ref |
|---------------|---------------|----------------|--------|------------|-----------|------------------------------------------------|-----|
| MWCNT         | fractionary-order model | Langmuir model | 5-7    | Fe$^{2+}$  | 253.38    | non-electrostatic π-π dispersion interaction | [2] |
| MWCNTs        | pseudo-second order |              | 4.5-7  |            |           |                                                 |     |
| MWCNTs        | pseudo-second order | Freundlich sorption model | 845.9  | C=O stretching vibrations | Van der Waals forces, π-π EDA interaction, cation-π bonding | [7] |
| MWCNTs        | pseudo-second-order |               | 3.3-8  | Cu$^{2+}$  | 269.25    | electrostatic interactions, π-π interactions and double bonds, hydrophobic interactions | [10] |
| (G-MWCNTs)    | Freundlich sorption model |              | Cu$^{2+}$ | Or Ni$^{2+}$ | 82.35     | Dispersive π-π adsorbate-adsorbent interactions, TCS dimensions | [12] |
| MWCNT/MIL-53(Fe) | pseudo-second-order | Langmuir equations |        |            | 99.4      |                                                 |     |

Table 1. Kinetics, adsorption isotherm, properties, mechanism, and maximum adsorption capacity
6. Reference

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