Adsorption characteristics of carbon nanotubes on low concentration erythromycin in water

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Abstract. Multi-walled carbon nanotubes (MWNTs) were used to adsorb low concentration erythromycin from natural water. The kinetic curves and adsorption isotherms were measured and the thermodynamic parameters were calculated. The effects of pH value, ionic strength and humic acid on the adsorption process were investigated. The results showed that the adsorption of carbon nanotubes to erythromycin was rapid in the first 40 min, and reached equilibrium within 200 min. The dynamics curve conforms to the quasi-second-order dynamics model. The Freundlich model can better fit the adsorption test data. Thermodynamic parameters show that the adsorption of Erythromycin by MWNTs is a spontaneous endothermic process. The adsorption activation energy Ea shows that the adsorption between MWNTs and erythromycin is a chemisorption process, and the content of oxygen-containing functional groups on the surface of CNTs determines the equilibrium adsorption amount. Ionic strength has obvious effect on adsorption. Increasing the pH value of the solution from 5 to 9 was beneficial to increasing the adsorption capacity of erythromycin. The adsorption capacity of carbon nanotubes to erythromycin was significantly increased with appropriate humic acid.

1. Introduction
Macrolides are one of the most effective antifungal antibiotics, which are widely used in the clinical and food industry. A large number of residual antibiotics enter the environment in the form of excreta and pose a serious threat to the ecosystem and human health. It has been reported that long-term exposure to antibiotics in natural water may cause people to suffer from acute and chronic diseases and cause the microorganisms in the environment to produce antibodies, leading to the failure of antibiotics in clinical application[1]. At present, more attention is paid to the priority control pollutants and the enrichment and treatment of trace heavy metal pollutants in the treatment of natural water pollutants. Foreign studies have shown[2] that adding a biofilm pretreatment system in front of the conventional treatment of water plants can effectively remove organic pollutants in slightly polluted water, but the biofilm is easy to fall off partly and cause secondary pollution to the source water. Domestic research on antibiotics is still mainly focused on the enrichment, separation and purification of high-concentration antibiotic production wastewater[3-4], while the removal of low-concentration
antibiotics in natural water is far from meeting the requirements of human health, both in theoretical research and in water treatment practice technology. Therefore, it is necessary to study the removal of macrolide antibiotics represented by erythromycin in low concentration water.

Carbon nanotubes (CNTs) have been used as adsorbents or carriers for the adsorption of inorganic and organic substances in water because of their high reactivity, high specific surface area and high specific surface energy. Carbon nanotubes have unique π electron, pore structure and adsorption properties. Studies have shown that [5-6]: carbon nanotubes have strong adsorption properties for chlorobenzene, trihalomethane, aniline, nitrophenol, heavy metal ions and other pollutants in water. The major limitations of large-scale use of carbon nanotubes for water purification technology are the efficient recovery of carbon nanotubes and the high operating cost. In terms of the mechanism of removal of organic matter by carbon nanotubes, hydrophobicity, hydrogen bonding, electrostatic interaction and π-π electron donor-acceptor are mainly involved [7-8]. At present, CNTs have not been used to remove low-concentration macrocyclic lipid antibiotics from water, nor is the adsorption properties of these compounds on CNTs known.

Based on the big ring inside lipid antibiotics, erythromycin as the subject matter of new adsorbents, multi-walled carbon nanotubes (MWNTs) and its oxides adsorbed water through the research of the performance of the low concentration of erythromycin is EM on the two kinds of adsorbent adsorption process, so as to remove carbon nanotubes in water low concentration of large ring lipid to offer reference to the research and application.

2. Materials and methods

2.1. Experimental materials and instruments

The multi-walled carbon nanotubes (MWNTs, model TNM3, 97% purity) used in the experiment were purchased from Chengdu Organic Chemistry Co., Ltd., Chinese Academy of Sciences. Erythromycin (purity >99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. The main experimental instruments and equipment are: high performance liquid chromatograph (model: Agilent 1100), etc. Treatment of carbon nanotubes: dilute concentrated nitric acid quantitatively to get 100 mL 3 mol/L nitric acid solution for the experiment, add appropriate amount of carbon nanotubes and ultrasonic vibration for 24 h, take them out for filtration, wash them with double steam water until neutral, and put them in the oven at 100°C for drying for 8 h[9].

2.2 Characterization of multi-walled carbon nanotubes

Three portions of 10 mg carbon nanotubes were accurately weighed and placed in a 50 mL beaker, and 20 mL NaHCO₃, Na₂CO₃ and NaOH solutions of 0.01 mol/L were added, respectively. The mixed solution was filtered through 0.22 μm polyethylene membrane and washed with distilled water. The whole titration process was titrated with 0.01 mol/L HCl solution. The end point was monitored with pH indicator. According to the Boehm acid-base titration theory, the weak base NaHCO₃ can only react with the surface carboxyl group. The neutral base Na₂CO₃ can react with surface lactone group besides carboxyl group. In addition to the above groups, strong base NaOH can also react with hydroxyl groups on the surface. The contents of various oxygen-containing functional groups on the surface of carbon nanotubes can be obtained by using the difference values of the three measured results.

The isoelectric point (pHZPC) was determined with a Zeta potential analyzer (Zetasizer Nano Z, Malvern, UK). Specific surface area and pore structure N2 adsorption-desorption isotherms were determined at 77 K using the Specific Surface Area and Pore Analyzer (AS-AP2020, Mick Corporation, USA). The specific surface area was calculated by BET method, and the mesopore volume was calculated by BJH method.
2.3. Analysis conditions
The concentration of erythromycin in the solution was determined by high performance liquid chromatography. The chromatographic conditions were determined as follows: column temperature 20℃; The flow rate was 0.5 mL/min, the detection wavelength was 210 nm, and the sample size was 20 μL. The mobile phase consisted of acetonitrile, methanol and 20 mmol/L ammonium dihydrogen phosphate buffer (the volume ratio of the three was 5:4:1), which was adjusted to neutral with triethylamine.

2.4. Experimental Methods

2.4.1. Adsorption kinetics test
The initial concentration of erythromycin solution was 20 μg/mL, 100 mL for each group. 10 mg carbon nanotubes and their oxides were accurately weighed and placed into the solution. Considering the acid-base characteristics of lightly polluted natural water, the samples were shaken and adsorbed at a constant temperature of pH=7.0±0.1 (298K) for 24 h. The remaining concentration of erythromycin was measured by chromatographic method at certain intervals.

2.4.2. Adsorption isotherm experiment
In the study of adsorption isotherm, 10mg carbon nanotubes were placed in different concentrations of Erythromycin solution and adsorbed for 24 h at pH=7.0±0.1 at 288K, 298K and 308K. Calculate equilibrium adsorption capacity (QE) according to formula (1)

\[
Q_e = \frac{(c_0 - c_e) V}{m}
\]

Where, QE -- equilibrium adsorption capacity (mg /g), CO and Ce -- initial and equilibrium solution mass concentration (g /L), V -- solution volume (mL), M -- carbon nanotube mass (g)

2.4.3. Single point adsorption test
To investigate the effect of pH, 10 mg carbon nanotubes were accurately weighed and added into the initial solution of 8 groups of erythromycin (pH of the solution was adjusted to 5-12 by 0.01 mol/ L HCl and 0.01 mol/ L NaOH). To investigate the effect of humic acid, 10 mg carbon nanotubes were accurately weighed and added into the initial solution of 6 groups of erythromycin (humic acid concentration was adjusted to 2, 5, 7, 10, 15 and 20 mg/L, respectively). To investigate the ionic strength, NaCl was used to simulate the effect of the monovalent ion Na⁺ in water, and 30mg was accurately weighed and put into the initial solution of 6 groups of erythromycin (adjusted to 0, 0.1, 0.3, 0.5, 0.7 and 1.0 mmol/L). The initial concentration of EM in the single point adsorption experiment was 20 μg/mL, and the other experiments were the same as the adsorption kinetics experiment.

3. Results and discussion

3.1. Adsorption kinetics
Figure 1 shows the adsorption kinetics curve. In the first 40 min of the experiment, the adsorption was very rapid, reaching 87.98% and 82.52% of the maximum adsorption capacity, respectively. The adsorption equilibrium was basically reached at 200min, indicating that MWNTs achieved a good adsorption effect in a relatively short time. Studies have shown that in the initial stage of the adsorption process, porous substances are mainly adsorbed through pore filling, and the mesopore capacity can increase the initial rate of compound diffusion [12]. MWNTS1 has a larger mesopore volume, so it has a higher adsorption rate. With the extension of adsorption time, the equilibrium adsorption amount will change after various diffusion and chemical bond cooperation reach equilibrium.
3.2. Adsorption isotherm

The adsorption isotherm is shown in Figure 2, and the fitting isotherm model parameters are shown in Table 3.

The correlation coefficient $R^2$ of Freundlich model was 0.99, indicating that the adsorption process conforms to the Freundlich model. The $K_f$ fitted by Freundlich model increases from 122.98 to 146.13, and the characteristic constant $n$ increases from 2.104 to 2.378, indicating that adsorption becomes easier and easier, and increasing temperature is conducive to adsorption reaction. Studies show that the adsorption index $N$ value is generally between 0 and 10, when $N$ &gt; 1, it is favorable adsorption, and when $n$ &lt; 1, it is adverse adsorption. The characteristic constant $n$ in the experimental results is always greater than 1, indicating that carbon nanotubes are favorable for the adsorption of erythromycin.

The correlation coefficient $R^2$ of Dubinin-Radushkevich isothermal model fitting 0.96, indicating that Dubinin-Radushkevich model is also suitable for the isothermal adsorption of carbon nanotubes to erythromycin. Studies show that When the adsorption activation energy $E_a$ is 1-8 kJ·mol$^{-1}$, the adsorption is physical adsorption; When $E_a$ is 8-16 kJ·mol$^{-1}$, the adsorption process is adsorption. When the $E_a$ &gt; 16 kJ·mol$^{-1}$, the adsorption process was intra - particle diffusion. The calculated $E_a$ values were 11.76, 12.99 and 13.61 kJ·mol$^{-1}$, respectively, indicating that the adsorption of Erythromycin by CNTs was mainly a chemisorption process. Research shows that When PH &lt; 10 o ‘clock, the electron of erythromycin molecule is easily lost, which makes the molecule become a strong π-electron donor. The oxidized carbon nanotubes act as strong π-electron acceptors due to the carboxylated functional groups on the carbon ring, which enhances the π-π interaction between them.
3.3. The effect of pH

The effect of pH on the adsorption of EM on MWNTs was shown in Figure 3. The results showed that the adsorption capacity of Erythromycin by MWNTs increased rapidly with the increase of pH and reached a peak of 165.47 mg/g at pH=9. Compared with the adsorption capacity of 121.49 mg/g at pH=5, the adsorption capacity increased by about 36.2% and then decreased gradually.

In low pH value of solution on the adsorption of erythromycin because of lower might be: low pH in aqueous solution, there are abundant hydration protons (H$_3$O$^+$), the surface of carbon nanotubes are rich in electronic PI adsorption lack of H$_3$O$^+$ protons, formed on the surface of positive charge, and erythromycin ionization ion like charges the repulsion between the results in the decrease of the adsorption quantity. In addition, the study shows that when PH$>10.0$, Em mainly exists in free molecular state, which may be the reason that higher pH is not conducive to adsorption. Therefore, when the pH is between 5.0 and 9.0, the EM equilibrium adsorption capacity increases with the increase of pH value and reaches the maximum near 9.0.

![Figure 3 Effect of pH value on absorption of Erythromycin](image)

4. Conclusion

(1) Carbon nanotubes can effectively adsorb erythromycin. 40 min before adsorption is a rapid adsorption stage, which can reach 80% of the maximum adsorption capacity, and the adsorption reaches equilibrium within 200 min. After oxidation, the equilibrium adsorption capacity can reach 143.57 mg/g at 298K and pH=7.0±0.1. The parameters of particle internal diffusion model show that the adsorption process is controlled by particle internal and external diffusion, and the adsorption kinetics conforms to the quasi-second-order kinetics model. The Freundlich adsorption isotherm model was used to describe the adsorption isotherm. Thermodynamic parameters proved that the adsorption of erythromycin by MWNTs was a preferential adsorption process, which was spontaneous endothermic reaction and non-uniform adsorption. The adsorption activation energy Ea showed that the adsorption between MWNTs and Erythromycin was a chemisorption process, and π-π electron donor-acceptor interaction might be the main mechanism of carbon nanotubes adsorption of Erythromycin.

(2) Compared with the carbon nanotubes before and after nitric acid oxidation, the equilibrium adsorption capacity of carbon nanotubes increases with the increase of oxygen-containing functional groups. Single-point experiments showed that the effect of pH value on the adsorption capacity increased firstly and then decreased, and the maximum adsorption value reached around pH=9.0, which was about 36.2% higher than that at pH=5. When the concentration of Na$^+$ reached 1.0 mmol·L$^{-1}$, the removal rate of EM by MWNTs decreased by nearly 2/3 compared with that under the same conditions. When the concentration of humic acid reached 7 mg/L, the adsorption effect was the best, and the adsorption capacity was increased by 13.6% under the same conditions.

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