

Adsorption Performance of Roxithromycin on Multi-walled Carbon Nanotubes in Water

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Abstract: The adsorption of roxithromycin from aqueous solution onto multi-walled carbon nanotubes was studied. The gravimetric method can be adopted for calculating the adsorption isotherm and kinetic curves of roxithromycin onto the carbon nanotubes. The influential factors including the pH and humic acid on the adsorption efficiency were investigated in the paper. Experimental results indicated that the adsorption kinetics and isotherm can be well described by using a pseudo-second-order rate model and Freundlich isotherm, respectively. The adsorption capacity of roxithromycin decreased with the addition of erythromycin in water. The adsorption capacity of roxithromycin decreased when the pH was less than 4 while adsorption capacity increased when the pH more than 4. The promotion action of the adsorption of roxithromycin onto multi-walled carbon nanotubes happened when the concentration of humic acids was less than 25mg/L while the inhibition action happened when the concentration of humic acids was more than 25mg/L.

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The extensive use of antibiotics has been paid much more attention in the fields of medicine, livestock breeding and aquatic product. It has been reported that the total usage of antibiotics was about 162, 000 tons in China in 2013^[1,2]. The majority of antibiotics are poorly adsorbed and thus excreted by humans or animals in faeces and urine, and can directly enter natural waters and soil. Moreover, the wastewater generated by the manufacturing operations of the pharmaceutical industry could be discarded into natural water systems^[3,4]. Conventional treatment process hardly remove or degradation the antibiotics in water and wastewater^[5-7]. The pollutants pass through the water and wastewater treatment processes, enter into the aquatic environment and subsequently threaten aquatic ecology, drinking water security and human health^[8-11].

Macrolides are synthetic broad-spectrum antibiotics commonly used in human and medicine treatment. They belong to one of the most commonly used families of antibiotics, although occurrence of macrolides in aquatic environment is at low concentrations, due to their poor water solubility^[12]. Roxithromycin is one of macrolides antibiotics, which was frequently found in water because of extensive usage, large production, long half-life period. The quantity order of roxithromycin of $\mu\text{g/L}$ was often detected in Germanic ground water and wastewater plant. Xu Huaihai found that roxithromycin concentration ranked highest on antibiotics indicator in the detection of pearl river quality^[13]. It is necessary to removal macrolides antibiotics such as roxithromycin in water.

Carbon nanotubes with high specific surface area and bound micropore are widely applied at environment protection field which has better adsorption capacity than activated carbon. Researches^[14] indicated that carbon nanotubes have strong adsorption capacity on varieties types of pollutants such as chlorobenzene, trihalomethane, phenylamine, nitrophenol and heavy metal ions et al. Li^[15] and Wang^[16] et al found that carbon nanotubes have excellent adsorption capacity which can fit Langmuir and Freundlich adsorption isotherm well by studying Pb^{+} adsorption efficient on

carbon nanotube in water. Shen Xiu'e^[17] regarded that carbon nanotubes could reach the adsorption balance in short interval accordance with pseudo-second order kinetics which adsorbed the antibiotics of sulfathiazole and ciprofloxacin. Currently, seldom references about roxithromycin adsorbed by carbon nanotube were reported.

The objectives of this study are to (1) investigate the roxithromycin sorption capacity and reaction kinetics on multi-walled carbon nanotubes; (2) found the effect of the erythromycin on roxithromycin removal efficiencies on multi-walled carbon nanotubes; (3) determine the effects of pH and HA.

Materials and Methods

Materials

Roxithylamine, ammonium dihydrogen phosphate, HCl and NaOH were analytical reagent, some chemicals were chromatographically reagent such as acetonitrile and methyl alcohol. Ultrapure water supplied was used to prepare all the reagents and solutions.

Pretreatment of multi-walled carbon nanotubes

Some quantity multi-walled carbon nanotubes were immersed into the 250mL of nitric acid (3 mol/L) in 500 mL flask at room temperature, shaken 24h with ultrasound, then washed with ultrapure water to neutral pH and dried in an oven at 393K for 8 h, furthermore, crushed into 0.001mg powder.

Adsorption kinetic and isotherm experiment

The experiments were carried out in a set of 250 mL erlenmeyer flasks with the addition of 100 mL of 20 mg/L roxithromycin or both 20 mg/L roxithromycin and erythromycin solutions and 50mg MWCNT. The suspensions were shaken on an orbit shaker at 180 r/min for hours at 298 K. The mixture was filtered through 0.45 μ m membrane. The filtrate was analyzed with HPLC. The quantity of removal roxithromycin was calculated by the difference of the initial and residual amounts of roxithromycin in solution divided by the weight of the adsorbent.

The concentration of roxithromycin was analyzed by the high performance liquid chromatography (HPLC) at a 210-nm wavelength. The apparatus was configured with Waters 2695 dual wavelength detector, Waters 717 Plus automatic sampler and Waters 1525 pumps. Roxithromycin was separated by C₁₈ column (150mm \times 4.6mm, 5 μ m Waters).

In order to study the adsorption isotherm of roxithromycin on the MWCNT, some initial roxithromycin concentrations were prepared and 50 mg MWCNT was added into each flask covered with glass stopper and the flasks were then placed in shaker until equilibrium point was reached. In this case, the solution pH was kept original without any pH adjustment.

Influence factors experiment

Experiments to determine the effect of solution pH values on roxithromycin removal were performed by adding 100 mg of MWCNT into the vessel containing 100 mL of 20 mg \cdot L⁻¹ roxithromycin solution. The pH of the solutions was adjusted with 0.01mol/L HCl and NaOH to designated values in the range of 1–11.

Experiments determining the effect of HA on roxithromycin removal were performed by adding 100 mg of MWCNT into the vessel containing 100 mL of 20 mg \cdot L⁻¹ roxithromycin solution at 298K with 3-80mg/LHA. The suspensions were shaken on an orbit shaker at 180 r/min for 4h at 298 K and filtered through 0.45 μ m membrane. The filtrate was measured with HPLC and pH and HAc effect on roxithromycin adsorbed by MWCNT were analysed.

Results and Discussion

Adsorption kinetics

The adsorption kinetics describe the rate of roxithromycin uptake on the MWCNT, which controls the equilibrium time. The kinetics parameters are helpful for the prediction of adsorption rate, which gives important information for designing and modeling the processes. The kinetics of the adsorption data were analyzed using different kinetics models: pseudo-first-order equation, and pseudo-second-order equation .

Pseudo-first-order equation is the most popular kinetics equation. The form is:

$$\log(q_t - q_e) = \log q_e - k_1 \cdot t / 2.303 \quad (1)$$

pseudo-second-order equation:

$$t/q_t = 1/v_0 + t/q_e; \quad v_0 = k_2 \cdot q_e^2 \quad (2)$$

where q_t (mg/g) is the mass of metal adsorbed at time t (min) and q_e (mg/g) is the mass of metal adsorbed at equilibrium; k_1 (/min), k_2 (g/(mg·min)), k_3 (mg/(g·min)) are the rate constants of the equation.

The kinetic curve of roxithromycin alone (Fig 1) showed that the adsorption rate was faster in 100min, then with the increase of adsorption capacity, the adsorption balance reached at 120min.

At the start of the adsorption, roxithromycin firstly adsorbed to the external cavity surface of the carbon nanotubes, adsorption capacity gradually rise, after the outside surface adsorption was saturate, and pass into the inner surface of the carbon nanotube until adsorption saturation. The experimental data were fitted with the model of the quasi-first and second-order dynamics model, and the results were shown in table 1:

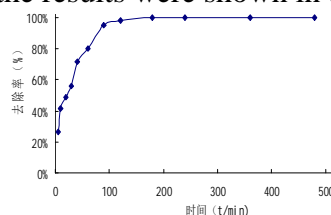


Fig.1 Effect of time on roxithromycin

Table1 The kinetic model fitting equations and parameters

kinetic model	fitting equation	k (g·mg ⁻¹ ·h ⁻¹)	R ²
pseudo-first order rate	$\ln(q_e - q_t) = -0.0316t + 3.649$	1.8932	0.9835
pseudo-second order rate	$t/q_t = 0.0239t + 0.0064$	0.0893	0.9984

According to Tab.1, the linear correlation coefficient of roxithromycin was greater than 0.98, and the whole adsorption process of carbon nanotube with roxithromycin was better described by the quasi-second-level dynamic model. Fig.2 is

the adsorption kinetics curve of erythromycin and roxithromycin in water. It can be seen that erythromycin had a faster adsorption rate than roxithromycin and can reach the adsorption equilibrium earlier. roxithromycin adsorption rate made slower when erythromycin coexisted in comparison with roxithromycin alone adsorbed by carbon nanotubes, It due to that erythromycin firstly occupied adsorption site on the surface of the carbon nanotubes and easier to enter the carbon nanotube cavity, so the rapid adsorption equilibrium reached.

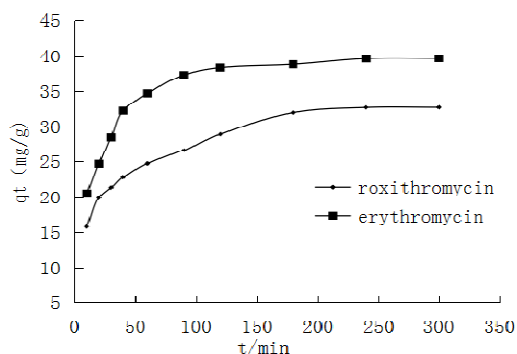


Fig.2 Effect of time on roxithromycin and erythromycin

From Tab.2, the linear correlation coefficient of two kinds of antibiotics were greater than 0.95, using the quasi-second kinetic model can well describe the adsorption process of roxithromycin and erythromycin on carbon nanotubes, Tab. 3 showed that the adsorption rate constant of roxithromycin was lower when erythromycin coexisted than that of the roxithromycin exist alone.

Adsorption isotherm

Here the adsorption of roxithromycin on the surface of MWCNT was investigated. In this study, Langmuir and Freundlich adsorption isotherm were applied to fit the equilibrium data of adsorption of roxithromycin on the MWCNT. The linearized form of Langmuir equation is defined as the equation (3). The Freundlich model is formulated as the equation (4).

$$1/Q_e = 1/(bQ_0C_e) + 1/Q_0 \quad (3)$$

$$\log Q_e = \log k + 1/n \cdot \log C_e \quad (4)$$

Where Q_e is the amount of solute roxithromycin adsorption on the adsorbent surface ($\text{mg} \cdot \text{g}^{-1}$), C_e is the equilibrium concentration of roxithromycin in the solution ($\text{mg} \cdot \text{L}^{-1}$), Q_0 is the maximum surface density at monolayer coverage and b is the Langmuir adsorption constant ($\text{L} \cdot \text{mg}^{-1}$). k is Freundlich constant ($\text{mg} \cdot \text{g}^{-1}$) and n is the heterogeneity factor.

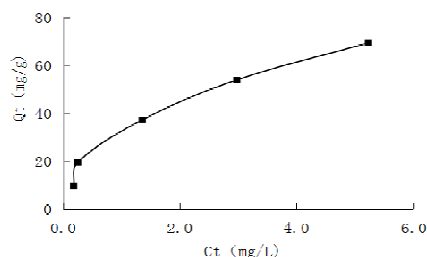


Fig.3 Adsorption isotherms of roxithromycin

Fig.3 illustrated the adsorption isotherm of roxithromycin on MWCNT. All the correlation coefficient, R^2 values and the constants obtained from the two isotherm models applied for adsorption of roxithromycin on the MWCNT were summarized in Tab.3. The Freundlich model fitted the experimental data as well as the Langmuir model, both were 0.95. This suggested that some heterogeneity on the surfaces or pores of the MWCNT played the role in roxithromycin adsorption. Tab.3 also listed the maximum monolayer adsorption capacity 84mg/g of roxithromycin on MWCNT.

Table 2 The quasi-second kinetic model fitting equations and parameters

antibiotic	Fitting equation	$K(\text{g} \cdot \text{mg}^{-1} \cdot \text{h}^{-1})$	R^2
roxithromycin	$t/qt = 0.0251t + 0.8105$	0.0474	0.9791
erythromycin	$t/qt = 0.0251t + 0.0526$	0.7216	0.9999

Table3 The parameters of Freundlich and Langmuir equation based on static adsorption data

T	Freundlich			Langmuir		
	n	K_F	R^2	X_m	a_1	R^2
298	1.9069	30.2883	0.954	84.0336	0.8264	0.951
			2			5

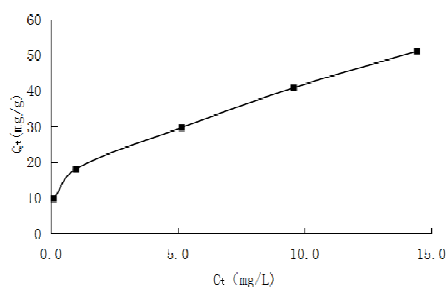


Fig. 4 Adsorption isotherms of roxithromycin

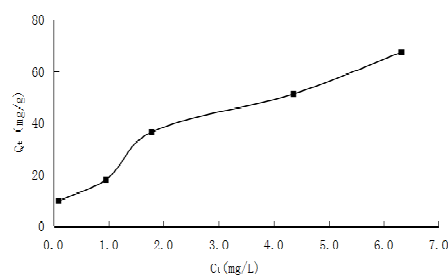


Fig.5 Adsorption isotherms of erythromycin

Table 4 The Freundlich equation and parameters of erythromycin and roxithromycin

antibiotic	Fitting equation	n	K _F	r
erythromycin	$\text{Ln}Q_e = 0.2686 \text{Ln}C_e + 2.9606$	3.7194	18.9276	0.9702
roxithromycin	$\text{Ln}Q_e = 0.4641 \text{Ln}C_e + 3.5503$	2.1547	33.9994	0.9010

Fig.4 and Fig.5 illustrated respectively the adsorption isotherm of roxithromycin and erythromycin on MWCNT. Results showed that the adsorption capacity of roxithromycin on MWCNT obviously decreased when roxithromycin and erythromycin coexisted in the solution. The Freundlich model fitted the experimental data of roxithromycin and erythromycin, both were over 0.9. This suggested that Freundlich model could fitted well the adsorption process. K_F of roxithromycin was lower than K_F of erythromycin which indicated that adsorption strength on roxithromycin was less than on erythromycin. While the n was more than 1, the adsorption process was favorable adsorption.

Effect of pH

The chemical form of adsorbent and adsorbate would change with pH variation which influenced the adsorption performance. Fig 8. indicated that adsorption capacity decreased when $\text{pH} < 4$, While adsorption capacity increased when $\text{pH} > 4$, the adsorption capacity of 34.88mg/g was maximum when $\text{pH} = 11$. Roxithromycin was alkaline chemical which was unsteady and apt to hydrolysed in acid condition.

At $\text{pH} < 7$, the species of roxithromycin predominantly existed in ions. With the increase of pH value, the ions and molecule coexisted in water. At $\text{pH} > 9$, the species of roxithromycin predominantly existed in free molecule. The carboxyl group of carbon nanotubes was easy to generate hydrogen bonds under low pH value, and reduced the formation of hydrogen bonds under high pH value because of ionization. Adsorption performance of roxithromycin on carbon nanotubes enhanced because of hydrogen bonding production. Carbon nanotubes were positively charged in $\text{pH} = 1$, which can produce electrostatic attraction with negatively charged roxithromycin, further increased the adsorption capacity. With the increase of pH value, the role of the hydrogen bonds weakened gradually. The carbon nanotube surface was negatively charged, and repulsion effect happened with roxithromycin, which was not conducive to the adsorption and adsorption capacity therefore continue to decrease. When the $\text{pH} > 7$, because the roxithromycin free molecules increased, the mass transfer driving force increased, the absorption rate accelerated, thus improved the adsorption quantity.

Effect of HA

Fig 8. showed that roxithromycin adsorption on multi-walled carbon nanotube is slowly promoted by humic acid when humic acid concentration was lower than 25 mg/L, inhibition of multi-walled carbon nanotubes was found on roxithromycin adsorption when humic acid concentration was greater than 25 mg/L, roxithromycin adsorption capacity gradually reduce to the lowest level of 24.3 mg/g.

One of the reasons was that low concentration humic acid plays a role in the adsorption bridge, which increased the dispersion of nanometer materials in water, thus enhancing the adsorption effect. On the other hand, roxithromycin has very strong hydrophobicity, and the structure of the humic acid was favourable to adsorption of hydrophobic material. The lower oxygen content of humic acid, the less adsorption on hydrophobic new material [18].

Therefore, the adsorption of roxithromycin was promoted when the humic acid concentration was less than 25 mg/L. With the increase of humic acid concentration, humic acid and roerythromycin can produce competitive adsorption and compete with each other on the surface of multi-walled carbon nanotubes. Although humic acid has some adsorption capacity for roxithromycin, the surface area of humic acid is much smaller than the surface area of carbon nanotube, resulting in the decrease of roxithromycin adsorption.

Moreover, the adsorption capacity of roxithromycin was further reduced when the size of the humic acid molecule was larger and the larger surface area of the carbon nanotube was taken up. Humic acid containing negative charge, and the multi-walled carbon nanotube adsorbs humic acid, which increases the negative charge on the surface of the carbon nanotubes. There was negative charge on roxithromycin, so the electrostatic attraction between the carbon nanotubes and roerythromycin would be weakened [18].

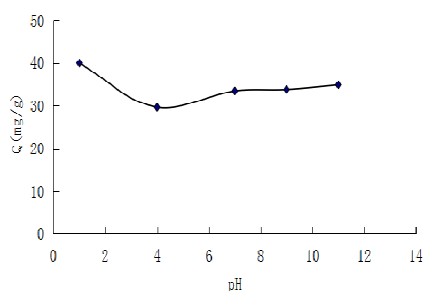


Fig.6 Effect of pH value on roxithromycin

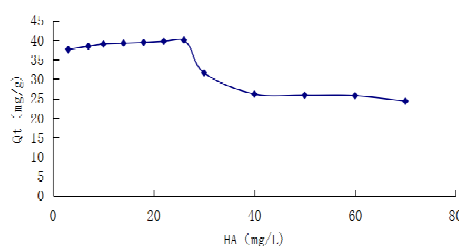


Fig.7 Effect of HA on roxithromycin

Conclusions

Multi-walled carbon nanotubes have good adsorption ability to roxithromycin, the process can be well fitted by the Freundlich isothermal adsorption equation. The kinetics of the adsorption process was found to follow the pseudo-second-order kinetic model with high correlation. When erythromycin coexists in the solution, the adsorption quantity and adsorption rate of roxithromycin were significantly reduced. The adsorption of roxithromycin on multi-walled carbon nanotubes was affected by pH value, and the adsorption of roerythromycin decreased gradually at $\text{pH} < 4$. The adsorption quantity of roerythromycin increased at $\text{pH} > 4$, when $\text{pH} = 11$, reached a maximum. The adsorption of roxithromycin on multi-walled carbon nanotubes was affected by the presence of humic acid, when the concentration of humic acid was less than 25 mg/L, the adsorption of roxithromycin on multi-walled carbon nanotubes was slow, when humic acid concentration was greater than 25 mg/L, the adsorption process was inhibited, adsorption capacity of roxithromycin on multi-walled carbon nanotubes gradually reduced.

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