Kinetic and thermodynamic analysis of adsorption of naproxen by activated sludge

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Abstract: Naproxen, a new environmental drug pollutant, shows “false persistence” in the environment and causes certain risks to human health and ecological environment, which has attracted extensive attention. The activated sludge in the sewage treatment technology plays a significant role in the control of the naproxen content. This paper carried out the kinetics and thermodynamic analysis of the adsorption process of naproxen by activated sludge. The experimental results show that the adsorption process of naproxen by activated sludge conforms to the pseudo-second-order kinetic equation and the linear fitting R² value is more than 0.99 at different initial concentrations. The Freundlich equation and Langmuir equation were adopted to carry out the adsorption models fitting. The Freundlich equation could represent the adsorption results satisfyingly. There is a negative correlation between the initial concentration of naproxen and the adsorption rate. The adsorption effect is determined by the hydrophobicity of naproxen and the electrostatic reaction between naproxen and activated sludge. After adsorption, there is no obvious naproxen desorption in activated sludge.

1. Introduction
As one kind of non-steroid anti-inflammatory and painkiller, naproxen is listed as the over-the-counter drug with antiinflammatory, antipyretic and analgesic effects. Due to its widespread use, naproxen is detected in various environmental media [1-5]. Although the new environmental drug pollutants are recognized by human beings earlier, they have attracted concern recently, which have certain risks to human health and ecological environment[6]. Without relevant laws and international conventions, those pollutants lack of regulation and control. The half-life of pollutants in environmental media is relatively long and they will cause false persistence phenomenon in the environment with the continuous use of human beings. The previous studies have shown that the probability of heart disease will increase significantly with the long-term intake of naproxen non-steroid anti-inflammatory painkillers [7-8].

Sewage treatment facility is the important means to control the entry of new pollutants into the environment [9-11], whose core technology is biological treatment. The traditional biological treatment technology mainly uses microbial metabolism to consume the organic pollutants in the wastewater, which only effectively removes the biodegradable organic pollutants [12]. In the early period, three sewage treatment plants in Guangdong Province, China, were sampled and investigated.
The results show that the sewage treatment plant has certain removal effect on naproxen, whose average removal rate reaches 50%. The sewage treatment plant is mainly realized by adsorption and biodegradation of activated sludge, and aerobic conditions are more beneficial to the removal of naproxen [13-15]. The further study on the removal mechanism of naproxen by activated sludge can provide a theoretical basis for the removal of pharmaceutical pollutants in sewage treatment plants and offer ideas to optimize the removal effect. This paper investigated the adsorption of naproxen by activated sludge in different water matrices and constructed the adsorption isotherm equation based on the concentration change of naproxen in aqueous phase. By the analytical experiments, the paper defined whether the activated sludge adsorbed with naproxen would cause environmental pollution again in the project of resource utilization, carried out the kinetic equation fitting of the adsorption process of naproxen by activated sludge under aerobic conditions, investigated the effects of different initial concentrations of log Kow and pKa on the adsorption process.

1. Materials and methods

2.1. Experiment material
The standard solution of Naproxen mother liquor was dissolved in methanol and stored at -20°C temperature, whose initial concentration was 100ppm.

Activated sludge: TSS of the mixture of mud and water in the biological aerobic tank of a municipal wastewater treatment plant in Guangzhou is in the range of 3.38~4.11g/L. The mixture of mud and water was used in adsorption and desorption experiment respectively after being concentrated.

The raw water used in kinetic experiment was artificial self-made wastewater with COD about 300mg/L. Different concentration gradients of Naphthalene wastewater were prepared by adding a certain amount of Naproxen mother liquor.

The raw water used in the adsorption isotherm experiment is divided into two kinds: one is the 1.5mM raw water (A) prepared from ultra-pure water containing sodium azide with different concentration; the other is the raw water (B) prepared from artificial self-prepared wastewater containing 1.5 mM sodium azide with different concentration. The raw water was stored in brown reagent bottle at 4 ℃ and set aside.

2.2. Experiment methods
(1) Kinetic experiment
In the process of adsorption kinetics experiment, 1g sodium azide was added to the reaction system (1L beaker) to inhibit the biological activity of activated sludge and shield the biodegradation, which simply reflected the adsorption of naproxen by activated sludge. The 0.3L sludge was placed in 1L beaker and raw water with different concentration gradients was added. The experiment was carried out at room temperature. The experimental process was stirred by magnetic agitator, the rotating speed was 500~600r/min and the total reaction time of adsorption test was 60 min. In the whole experiment process, there are blank experiment and parallel group experiment, and the data used in the analysis are the average value after deducting the blank experimental value.

(2) Adsorption and desorption
The experimental concentration range was controlled in the adsorption isotherm test of 100ppb~1ppm: ①In the adsorption isotherm test experiment, 20mL activated sludge was placed in 50mL centrifugal tube, centrifuged to remove the culture medium with 1500r/min, added different concentration gradients of solution A and B to 20mL and mixed. The parallel test and blank test were carried out and the concentration of the culture medium was analyzed by centrifugation after the experiment was balanced. ② In the desorption experiment, the initial concentration of solution A and B was intermediate concentration. After mixed concussion and adsorption equilibrium, 5mL culture solution was obtained to analyze the concentration and then the solutions A and B, which did not contain the target pollutant in 5mL, were added and mixed. After equilibrium, 5mL of supernatant was removed.
to analyze the concentration, and then 5 mL of solution A, B without the target pollutant was added back. This operation was repeated. Additionally, two desorption solutions C and D were added, which were the influent and effluent of a sewage treatment plant, and the analysis of the target pollutants in four different water media was investigated.

Three groups of parallel tests were set up in the adsorption experiment and four groups of parallel tests were set up in the desorption experiment. The data used in the analysis process were the average values of the parallel experimental data.

2.3. Monitoring methods

At the sampling time set by the experiment, 1mL culture fluid was obtained and filtered by aqueous phase filter membrane (Anpel, Shanghai, China), whose material was 0.22μmPVDF. Then the culture fluid was transferred to the 2mL brown bottle and stored at 4 ℃ for HPLC (Agilent 1220). The analytical conditions were as follows: the column temperature was 35 ℃; the injection volume was 100μL; chromatographic column was EC-C18 (4.6×50 mm, particle size 2.7μm, Agilent); the UV detector was set at 230nm; the mobile phases A and B were dilute phosphate solution and methanol with the Ph of 3.0 respectively, whose flow rate was 1.0mL/ min; the gradient eluting was used. The retention time of naproxen was 5.3 min and the minimum on-board concentration of the standard curve was 1μg/L.

The pH values were measured by pH315i (WTW 82362 Weilheim, Germany) and the COD was measured by standard method (APHA-AWWA-WPCF, 2001).

3. Results and analysis

3.1. Kinetic analysis

The activated sludge is composed of bacteria micelle formed by a variety of microorganism, organic and inorganic substances adsorbed by it. The water content of activated sludge is high and the overall volume of activated sludge can reach tens of times as much as that of solid solvent. Therefore, the adsorption mechanism of activated sludge can be compared with that of porous media. The pseudo-first-order dynamic equation established in the course of previous research [14] and pseudo-second-order dynamic equation were used in the dynamic fitting equation:

\[
\log(q_t - q_e) = \log q_e - \frac{k_1}{2.303} t
\]

\[
t = \frac{1}{q_t} \left( 1 + \frac{1}{k_2 q_e} \right)
\]

Where \( t \) represents the reaction time for the adsorption of naproxen by activated sludge, whose unit is min. \( k_1 \) represents the constant of the primary adsorption rate, whose unit is \( \text{min}^{-1} \). \( k_2 \) represents the constant of the second adsorption rate, whose unit is \( \text{g/(µg·min)} \). \( q_t \) represents the amount of naproxen adsorbed by activated sludge at time \( t \) and its unit is \( \text{µg/g} \). \( q_e \) represents the maximum adsorption capacity of activated sludge for naproxen and its unit is \( \text{µg/g} \).

Table 1. The parameters determined from kinetic model in the adsorption experiments of naproxen by activated sludge.

| \( C_0 \) (µg/L) | Pseudo first-order | Pseudo second-order |
|-----------------|-------------------|--------------------|
|                 | \( k_1 \) (h\(^{-1}\)) | \( R^2 \)         | \( k_2 \) (h\(^{-1}\)) | \( R^2 \)         |
| 10              | 0.13              | 0.756              | 0.38              | 0.996              |
| 50              | 0.11              | 0.950              | 0.08              | 0.995              |
| 100             | 0.09              | 0.831              | 0.05              | 0.993              |
| 150             | 0.13              | 0.981              | 0.03              | 0.994              |
| 200             | 0.10              | 0.892              | 0.02              | 0.990              |

The fitting parameters of the two dynamic equations are shown in Table 1. The fitting degree of pseudo-second-order dynamics is obviously higher than that of pseudo-first-order dynamics. The
linear fitting $R^2$ value is more than 0.99 at different initial concentrations. Therefore, the adsorption process of naproxen by activated sludge is more suitable to be described by pseudo-second-order kinetic equation. In Table 2, the maximum adsorption value calculated by pseudo-second-order kinetic equation is close to the measured adsorption capacity and the relative deviation is less than 5%.

Table 2. The parameters determined from kinetic model in the adsorption experiments of naproxen by activated sludge.

| Compound | Naproxen |
|----------|----------|
| $C_0$ (µg/L) | 10 | 50 | 100 | 150 | 200 |
| $q_e$ (µg/g) | | | | | |
| 1.77 | 6 | 11.07 | 16.38 | 20.02 |
| 1.81 | 6.19 | 11.27 | 17.04 | 20.49 |
| RD(%) | 2.26 | 3.17 | 1.81 | 4.03 | 2.35 |

* measured value.

3.2. Thermodynamic analysis

3.2.1. Adsorption isotherm

In order to make the adsorption of naproxen by activated sludge reach the adsorption equilibrium as much as possible, the mixed concussion time is 24 h. At the same time, naproxen was dissolved in ultra-pure water and self-made artificial wastewater respectively in order to determine the possible effect of matrix on the adsorption of naproxen by activated sludge in aqueous phase. The adsorption capacity of naproxen by activated sludge per unit mass at different initial concentrations in two aqueous solutions is shown in Figure 1. In the adsorption experiment, the concentration of activated sludge was 4g/L and the total mass was 80mg. From Figure 1, it is seen that there is no significant difference in the adsorption capacity of 80mg activated sludge for naproxen in the two aqueous solutions. The $q$ value of adsorption capacity of artificial self-made wastewater is slightly higher than that of ultra-pure water. The maximum difference of adsorption capacity of naproxen by activated sludge per unit mass appears at the initial concentration of 800ppb and the difference is 5.32µg/g. When the initial concentration of naproxen is 100ppb, the $q$ value (4.63µg/g) of ultra-pure water is slightly higher than that of artificial self-made wastewater (4.12µg/g). The adsorption capacity of unit mass activated sludge for naproxen increases with the increase of initial concentration of naproxen. There is a positive correlation between $q$ and $C_0$.

![Figure 1. Adsorption capacity per unit mass of activated sludge under different initial concentrations of naproxen.](image)

The adsorption isotherms of the experimental results are further fitted. Freundlich equation is an
empirical adsorption model widely used in the field of environmental chemistry. The major
shortcoming of Freundlich equation is that it cannot predict the maximum adsorption capacity \( q_m \), but it
can represent the adsorption results more satisfactorily at the low concentration. Another widely
used adsorption model is Langmuir equation, which can describe adsorption and precipitation at
the same time. For the activated sludge of adsorbents in this experiment, adsorption and precipitation play
a leading role in the removal of activated sludge at the same time. Combined with the adsorbents in
this experiment, the adsorbents are trace pollutants, so the Freundlich equation and Langmuir equation
are used to fit the adsorption model at the same time.

The adsorption isotherm fitting of naproxen by activated sludge is shown in Figure 1. The fitting
curves of Freundlich equation are shown in Figure 2a and Figure 2c. The fitting curves of Langmuir
equation are shown in Figure 2b and Figure 2d. From the figure, it is seen that the fitting degree of
Freundlich equation is obviously better than that of Langmuir equation. In the medium of self-made
artificial wastewater, the \( R^2 \) values of Freundlich equation and Langmuir equation are 0.994 and
0.8227 respectively while in the ultra-pure water medium, the \( R^2 \) values of Freundlich equation and
Langmuir equation are 0.9977 and 0.8287 respectively. Therefore, the adsorption of naproxen by
activated sludge is more in line with Freundlich adsorption isotherm. Moreover, the adsorption
isotherms are not affected by two different aqueous solution conditions and the fitting degree of
Freundlich equation is always better than that of Langmuir equation.

![Figure 2. Adsorption isotherms on activated sludge in Milli-Q water](image)

The Freundlich fitting equation under the condition of ultra-pure water is shown as follows:

\[
y = 0.8004x - 0.8507
\]

The Freundlich fitting equation under the condition of self-contained artificial wastewater is shown
as follows:

\[
y = 0.8733x - 1.023
\]

Under two kinds of water quality conditions, the distribution coefficient \( K_d \) is 0.141 (ultra-pure
water) and 0.095 (self-made artificial wastewater). The correction factors \( n \) are 1.25 (ultra-pure water)
and 1.12 (self-made artificial wastewater), respectively. Yu et al. [16] also used Freundlich equation to fit the adsorption of naproxen by activated carbon. The results showed that the adsorption of naproxen by activated carbon was in accordance with Freundlich equation. Freundlich equation was first used in gas phase adsorption and solute adsorption. It is an empirical adsorption model widely used in the field of environmental chemistry. At low concentration, the Freundlich equation can express the adsorption results with satisfaction. As the new trace pollutant, naproxen mainly appears at the concentration level of ppt–ppb in environmental media. Therefore, the Freundlich equation has universal applicability.

3.2.2. Desorption
Most of soil environmental studies focus on adsorption so that the study of a target pollutant focuses on the adsorption properties of the target. However, it is also worth studying the desorption process. The pollutants in the soil will return to the water environment by desorption, resulting in the secondary pollution of the environment. In the actual application of water treatment, the adsorption material is used to remove the target pollutants. If the target pollutants are desorbed in the process of treatment and disposal of adsorbed materials, the purpose of truly effective removal of pollutants cannot be achieved.

In general, the desorption process is much more difficult than the adsorption process and not all the adsorbed pollutants can be desorbed, that is to say, the reaction process is irreversible. Irreversibility is usually referred to the hysteresis. Although adsorption occurs in the short time and it is completed, this completion process is for adsorbates (target pollutants) and it is ongoing for adsorbents. Some researchers have made the researches and found that 100min is sufficient to remove EDB added in the newly contaminated soil for the soils newly contaminated with 1, 2-dibromomethane (EDB) (balance 3 h) and soils contaminated by EDB for many years. However, for the latter only 5% of the original EDB is removed, which is typical of the effect of time on desorption. Therefore, the short-term laboratory studies cannot predict the adsorption-desorption behavior of pollutants accurately. However, many of the indexes currently used by regulators to evaluate criteria, such as distribution coefficients, are obtained from short-term balance experiments.

![Figure 3. The change of adsorption capacity per unit mass of activated sludge in desorption process](image)

To investigate the possible effect of matrix on desorption of Naphthalene by activated sludge in aqueous phase, four kinds of solutions were selected for desorption experiment. Four times of desorption were carried out and the experimental results are shown in Figure 3. From the results, it is seen that the desorption of naproxen in four kinds of water media is not obvious. After four times of desorption, the cumulative desorption rate is 5.1% ultra-pure water, 5.7% STP influent water and 9%
STP effluent. However, there is also a phenomenon of further adsorption in self-made water. Figure 3 is drawn based on the average value obtained from four parallel experimental data. In the process of the experiment, only one group of data shows desorption phenomenon in the desorption experiment with self-made water as desorption solution and its desorption rate is 4.6%. The other three sets of data show the hysteresis of desorption, which makes naproxen further adsorbed by activated sludge. The hysteresis is more common in the adsorption. There are many reasons for the detection of hysteresis, including artificial experimental conditions, chemical and microbial transformation during specific experiments.

3.3. Analysis of influencing factors of adsorption

After further analyzing the experimental data, the experiment clarified the relationship between the initial concentration of target pollutants and the adsorption rate of activated sludge. The linear fitting between the adsorption rate constant and the initial concentration of naproxen is shown in Figure 4. From the distribution of the midpoint of the graph, it can be found that there is obvious inconsistency between the distribution trend of the point when the initial concentration is less than 50ppb and when the initial concentration is greater than 50ppb. It is inferred that the removal mechanism of activated sludge will be different based on the concentration range of target substrate in the process of adsorption of PPCPs. Therefore, when the rate constant is linearly fitted with the initial concentration of the substrate, it should be divided into high and low concentration regions for fitting. Due to the limitation of detection methods, the low concentration region in this experiment lacks the experimental data. Therefore, when the linear correlation is determined, the points of the default (real line) and the non-default (dotted line) minimum concentration 10ppb are fitted linearly.

From the fitting results between adsorption rate constant and initial concentration of substrate, it is found that there is a negative linear correlation between the adsorption rate constant and the initial concentration of the substrate. With the increase of initial concentration, the rate constant decreases. The linear correlation under different concentration gradients is different and the R2 value under the default minimum concentration is higher than that without default. Therefore, it is unreasonable and unscientific to evaluate the degradation at low concentration according to the degradation kinetics equation of high concentration [16]. In the experimental analysis of adsorption of PPCPs by activated sludge, the R2 value of naproxen increases from 0.6 to 0.8754. Therefore, the high and low concentration regional segmentation point of 50ppb is suitable for naproxen. It should be noticed that
the activated sludge system is large and complex, which needs to be further studied to clarify the adsorption and removal mechanism.

The adsorption of target pollutants by activated sludge is mainly played by the hydrophobicity of the target and the electrostatic reaction between the target and the activated sludge. Hydrophobicity can be quantified by octanol-water partition coefficient (log K\text{ow}). For a given target pollutant, the log K\text{ow} of the compound is an important parameter to judge the adsorption degree of the adsorbed material. It is generally believed that the higher the log K\text{ow} value, the stronger the hydrophobicity of the target compound, and the greater the adsorption capacity of the target compound. In addition, it is also believed that the compounds with log K\text{ow} greater than 3 have the potential bioaccumulation. The log K\text{ow} value of naproxen is 3.18 (Data estimated from http://www.syrres.com), which can be effectively adsorbed by activated sludge. Under different pH conditions, (PPCPs) compounds of drugs and personal care products can exist in different forms in solution, including molecular, cationic, anionic or amphoteric ions. The forms mainly depend on the pK\text{a} value of the compound. The pK\text{a} value of naproxen is 4.15 (Data estimated from http://www.syrres.com). The pH value set by the experiment is 6.9 ± 0.1. Under the condition of this pH value, naproxen will hydrolyze and exist in aqueous solution in the form of anions. The microbial surface of the activated sludge has a negative charge. Therefore, under the experimental conditions, the adsorption of the target pollutants by the activated sludge will be hindered due to the electrostatic repulsive force between the target compound and the activated sludge. The experimental results show that naproxen can be adsorbed by activated sludge at various initial concentrations. Therefore, the adsorption resistance produced by electrostatic reaction is weaker than the adsorption thrust produced by hydrophobicity.

4. Conclusions
(1) The adsorption processes of the naproxen by activated sludge could be described by pseudo-second-order kinetic equation. As the new trace pollutant, naproxen is suitable for Freundlich adsorption isotherms generally in the process of adsorption by various adsorbents.

(2) After being adsorbed by activated sludge, the desorption effect of the naproxen is not obvious. Therefore, naproxen is not easy to cause secondary pollution of the environment during the treatment and disposal process of the surplus sludge.

(3) The adsorption rate constant and the initial concentration of the substrate have a negative linear correlation. With the increase of initial concentration, the rate constant decreases. The adsorption of target pollutants by activated sludge is mainly influenced by the hydrophobicity of the target and the electrostatic reaction between the target and the activated sludge.

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