

Thermodynamic Analysis of Pollution and Treatment of Organic Matter in Water

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Abstract: The problem of environmental pollution is becoming more and more serious with the rapid development of industry and economy, especially the organic matter pollution in water. Thermodynamic analysis method is used based on this to analyze and study the pollution and treatment process of water organic matter in this paper. By proposing that the pollution essence is caused by the uneven distribution of sub-energy, the effect of organic pollutants treatment in four kinds of water bodies in Shenzhen City was analyzed by graphite material adsorption from the perspective of thermodynamic analysis. The experimental results show that the degree of organic pollution in the Jia reservoir of Shenzhen City is from high to low: Dasha River, campus pond, Jia reservoir, and B reservoir. When the ionic strength is 0.04M, p H is 3.0, graphene loading is 2.5%, and SIS/RGO dosage is 200mg/L, the degradation efficiency of organic pollutants in water is as high as 96.25%.

Key words: Water body; Organic matter; Pollution; Governance; Thermodynamics

1. INTRODUCTION

Waste water from many industries such as agriculture, chemical industry and medical care has caused damage to the ecological environment and has attracted increasing attention worldwide, with the rapid development of industry and the strengthening of human activities, (Sung T et al. 2016) [1]. Organic pollution in urban waters is one of the most common environmental problems. The organic matter in water can be divided into exogenous organic matter (organic matter accepted by the water from the outside world) and endogenous organic matter (Li L et al. 2016) [2]. Exogenous organic matter includes organic matter leached from the soil by ground runoff and shallow groundwater, organic matter discharged into the water by urban sewage and industrial wastewater, organic matter washed out from the air by atmospheric precipitation, organic matter added to the water by surface aquaculture, etc. Endogenous organisms are derived from organic matter produced by biological groups (algae, bacteria, aquatic plants, and large algae) grown in water and organic matter released from water sediments. The source of organic pollutants (the type of organic pollution in water) is different, and the corresponding pollution control measures are different (Carcasci C et al. 2016) [3]. Therefore, it is necessary to fully understand the type of pollution of water bodies before conducting pollution control and treatment of water bodies. There are many methods and means for controlling organic pollutants. In summary, they can be divided into three categories: physical methods, chemical methods and biological methods. Although there are many studies on the ways of pollution, treatment

methods and environmental impacts of organic matter, there are few reports on energy conversion during pollution and treatment. (Shahin M S et al.2016) [4].

The method of treating organic matter in wastewater can be simply divided into physical methods, chemical methods, and biological methods. The energy changes and the transfer pattern are different if the treatment is different. Adsorption is caused by the intrinsic van der Waals force or hydrogen bonding of the adsorbent to allow contaminants to accumulate around the adsorbent from the water. The process is a process that consumes external energy. The external energy is used to overcome the increase of the system, and the energy of the pollutants and water itself does not change. It proposes that the essence of pollution is caused by the uneven distribution of sub-energy. Graphite material adsorption is used to analyze the effects of organic pollutants in four kinds of water bodies in Shenzhen through pollution and energy changes in treatment from the point of view of physical methods, with thermodynamic analysis methods. The application of this method is more efficient in degrading organic pollutants in water than in other methods.

The research in this paper is mainly divided into three parts. The first part summarizes the research status of the treatment of organic pollutants in water, and proposes that this paper will analyze the energy changes in pollution and treatment from the perspective of thermodynamics; The second part constructs a thermodynamic analysis method based on sewage treatment, and constructs the Gibbs free energy change function in the adsorption process to determine the degree of organic pollution of water bodies; In the third part, the adsorption of graphite materials is used to analyze the pollution of different water bodies and the energy changes in the treatment. The experimental results show that the 3DEEMs of the four different water bodies (Dasha River, Campus Pond, Jia Reservoir, and B Reservoir) have different contour maps and number of fluorescent peaks, and their peak positions and corresponding fluorescence intensity are also different.

2. STATE OF THE ART

The treatment of organic pollutants in water bodies is the focus and difficulty of environmental governance in recent years. Many scholars have conducted a lot of related research on their pollution and governance processes. Guo Y collected the water samples from the Hanjiang River in Wuhan during the wet and dry periods, and analyzed the organic composition of each sample by GC/MS. The results showed that the end water of the Han River was used as the water source, and 110 species and 102 species of organic matter were detected in the wet and dry periods respectively (Guo Y et al. 2016) [5]. Burlesonlesser K performs photocatalytic degradation of toxic and harmful organic wastewater by TiO₂ photocatalytic degradation, seawater desalination pretreatment and seafloor manganese nodules on organic pollutants. The research results provide valuable scientific theoretical basis and reference for industrial application in photocatalysis (Burlesonlesser K et al. 2017) [6]. Kim K H research believes that photocatalytic degradation technology provides a new and practical application value for organic wastewater treatment based on its broad-spectrum applicability and sensitivity to toxic organic compounds (Kim K H et al. 2018) [7]. Faleev V A summarizes the pollution status and treatment techniques of Persistent Organic Pollutants (POPs) in China's waters, and compares several treatment methods for POPs in water. The results show that China's water bodies have been polluted by POPs to varying degrees. The unpredictability of chemical degradation relative to the consequences of biodegradation and the incomplete degradation of physical methods have the characteristics of predictable results, controllable conditions, complete degradation, recycling of reagents and equipment,

etc., and have good feasibility (Faleev V A et al.2018) [8]. Lavarías S clarifies the synergistic effect of sunlight on organic pollutants in biodegradable lake waters, and compares the degradation under laboratory simulation conditions with the degradation under natural conditions, and proposes future development prospects and research directions in this field (Lavarías S et al.2017) [9]. Zeng Y uses quaternary ammonium salt cationic surfactant to graft and modify peat, and optimizes the modification conditions. The results show that the grafting amount of surfactant to peat increases with the modification time and the concentration of modifier (Zeng Y et al. 2016) [10]. In summary, it can be seen that the current pollution and treatment of organic matter in water has become the focus of academic research. It attempts to analyze the energy changes in pollution and treatment in this paper from the perspective of thermodynamics.

3. METHODOLOGY

3.1 Thermodynamic analysis based on pollution treatment

Chemical treatment of organic pollutants is generally carried out into a sewage into a substance, so that a chemical reaction occurs, destroying the molecular structure of the pollutants, forming a precipitate or being oxidized into a lower energy, which can be contained in the water environment. The oxidizing agent added is usually O_2 , O_3 , H_2O_2 , $Ca(ClO)_2$ and the like. This process is a process of releasing energy. Just as the ethylene glycol described in the "Contamination Process" is oxidized, the theoretical energy of the released energy can be theoretically calculated using the basic laws of thermodynamics and data. It is also possible to predict changes in the likelihood and reaction limits of the support, which has been thoroughly studied in numerous chemical equilibrium theories and will not be repeated.

Microbial treatment of sewage, Gibbs free energy change during adsorption (ΔG^0) is calculated by formula (1):

$$\Delta G^0 = -RT \ln k \quad (1)$$

In the formula, R is an ideal gas constant (8.314 J/mol. K), and k (mL/g) is a Langmuir isotherm adsorption constant at a certain temperature, and is obtained by converting K: units into ml/g. (ΔG^0) can also be used as a function of enthalpy change (ΔH^0), entropy change (ΔS^0) and temperature, and its expression is shown in formula (2):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (2)$$

Based on the assumption that (ΔH^0) and (ΔS^0) do not change with temperature over a small temperature range, (ΔG^0) can be considered as a linear function of temperature T. The calculated values are -24.3, -25.8 and -28.3 kJ/mol at 298, 308 and 318K, respectively. Typically, the value of (ΔG^0) is between 0 and -20 kJ/mol, the adsorption process is considered to be physical adsorption, and between -80 and -400 kJ/mol, it is considered a chemisorption process. In this study, (ΔG^0) is between physical adsorption and chemical adsorption, indicating that the adsorption of TC by ERG5 is a spontaneous physico-chemical adsorption. The value of (ΔH^0) is positive at 34.4 kJ/mol. It is known that TC adsorption to ERG5 is an endothermic process, mainly because ERG5 requires a certain activation energy for the dissociative chemisorption of TC. In addition, the value of (ΔS^0) for

ESG5 adsorption to TC was 196.8 J/(K.mol), indicating that the randomness of the solid-liquid interface increased during TC adsorption.

Studies on dissolved organic matter in rivers, lakes, and wetlands have shown that dissolved organic matter of different origins has different fluorophores, and the positions and fluorescence intensities of fluorescent peaks are also different. In general, the location of the fluorescent peaks of various dissolved organic matter in the natural environment can be summarized as follows (Figure 1): Class I (E_x is about 350~440nm, E_m is about 430~510nm); Class II (E_x is about 310~360nm, E_m is about 370~450nm); Class III (E_x is about 240~270nm, E_m is about 300~350nm); Class IV (E_x is about 240~270nm, E_m is about 370~440nm). Class I is humor-like. Class II and Class IV are visible fulvic-like and UV fulvic-like. Class III is protein-like. Since microbial-derived organisms have strong protein-like fluorescence, the fluorescence peaks of terrestrial organisms mainly appear in Class I and Class II positions. In this way, we can use 3DEEM to distinguish the source and composition of organic matter, and use the fluorescence intensity of the fluorescent peak to judge the degree of organic pollution of the water.

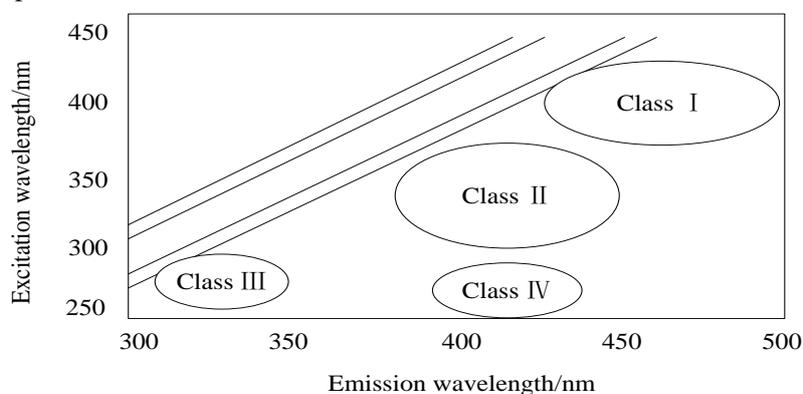


Fig. 1 Position of peak in 3-D fluorescence spectrogram

4. RESULT ANALYSIS AND DISCUSSION

The effects of different initial concentrations of TC (50~350mg/L) on adsorption were investigated at 293, 300 and 313K in this chapter. As shown in Figure 2, the amount of adsorption of ERG5 to TC increased significantly with the increase of initial concentration. This is because the higher initial concentration of TC can provide a stronger adsorption driving force and promote the diffusion of TC molecular mass transfer to the surface of ERG5. At the same time, as the temperature of the solution increases, the adsorption amount of TC increases, indicating that TC adsorption is an endothermic reaction process, and high temperature is beneficial to enhance the van der Waals interaction dipole moment between TC and ERG5, thereby promoting the adsorption process.

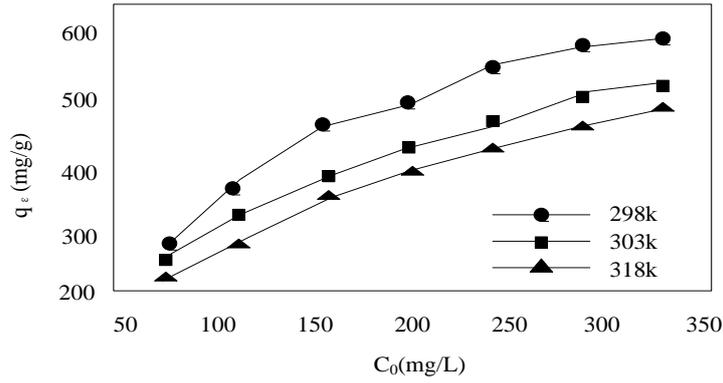


Fig. 2 Effect of temperature and initial concentration on adsorption of TC on ERG5

Figure 3 and Figure 4 show the effect of adsorption time on the adsorption of TC to the surface of ERG5 under different initial concentrations of TC. It can be seen that the removal of TC is a rapid adsorption process, and the adsorption curve tends to be balanced within 10 min, indicating that ERG5 is a fast and efficient adsorbent. In addition, pseudo first-order reaction kinetics and pseudo second-order reaction kinetics models were used to analyze the adsorption process of TC, and the corresponding equations are shown in equations (3) and (4), respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where q_e and q_t are the adsorption capacities (mg/g) $k_1 (h^{-1})$ and $k_2 (g/mg.h)$ of ERG5 in adsorption equilibrium and time t , respectively, are pseudo first-order reaction kinetics and pseudo second-order reaction kinetic constants.

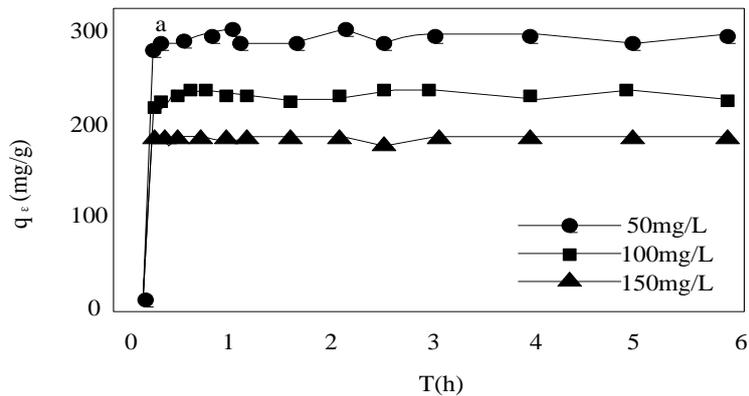


Fig. 3 Effect of adsorption time at different concentration

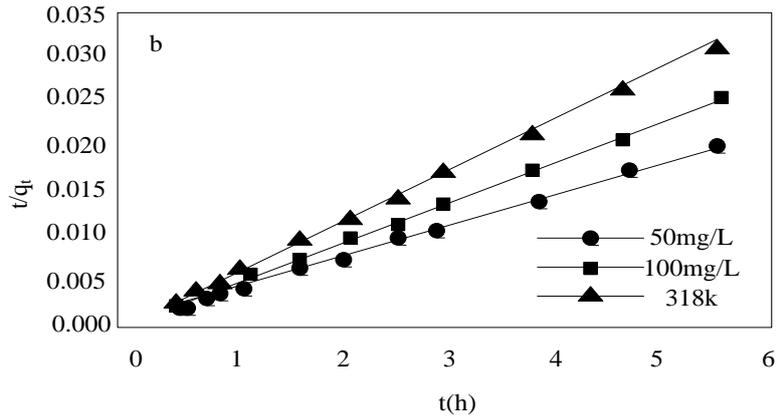


Fig. 4 Pseudo-second-order dynamic model

Table 1 Calculated values of kinetic parameters for TC adsorption on ERG5

Kinetic equations	parameter	TC initial concentration (mg/L)		
		50	100	150
Pseudo first-order reaction kinetics	$q_{e,exp}(mg/g)$	195	248	317
	$k_1(1/h)$	0.09	0.19	0.20
	$q_{e,cal}(mg/g)$	8.93	12.82	15.28
	R^2	0.03	0.11	0.11
Pseudo second-order reaction kinetics	$q_{e,exp}(mg/g)$	195	248	317
	$K_2(g.mg^{-1}.h^{-1})$	1.67	0.51	0.19
	$q_{e,cal}(mg/g)$	188.68	241.55	307.00
	R^2	0.99	0.99	0.99

The linear fitting parameters of the two models are shown in Table 1. By comparison, it is found that the pseudo second-order reaction kinetics can well describe the adsorption process of TC on the surface of ERG5, and the linear fitting coefficient R^2 is close to 1. And the experimental value $q_{e,exp}$ of the maximum adsorption amount of TC is very close to the calculated value $q_{e,cal}$. As the concentration of TC increased, the value of k_2 decreased from 1.67 to 0.19 g/m.h, indicating that the competitive adsorption between TCs increased sharply as the concentration of TC increased. In addition, the good linear fit of the pseudo second-order reaction kinetic equation to the t/q_t and t curves is shown in Figure 3 and Figure 4. Based on the assumption of the pseudo second-order reaction kinetic equation, the rate limiting mechanism of ERG5 adsorption to TC is mainly a chemical process through electron sharing or electron transfer. In order to study the isothermal adsorption behavior of ERG5 on TC, Langmuir, Freundlich, Tempkin and Hill adsorption isotherms were used to analyze the adsorption process. The Langmuir adsorption isotherm model assumes that the adsorption process is a single-layer adsorption occurring on a uniform surface, and the Freundlich adsorption

isotherm model is an empirical formula based on the adsorption process occurring on an uneven surface. The Temkin adsorption isotherm model assumes that there is an indirect interaction between the adsorbents during the adsorption process, and the adsorption heat decreases linearly with the change of surface coverage due to the existence of this interaction.

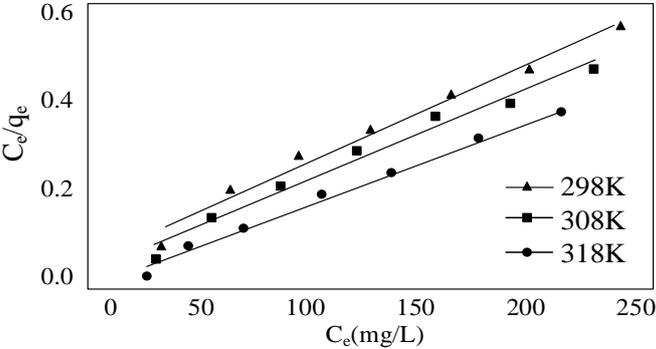


Fig. 5 Isothermal Linear Chart of TC Adsorption by ERG5 in Langmuir Model

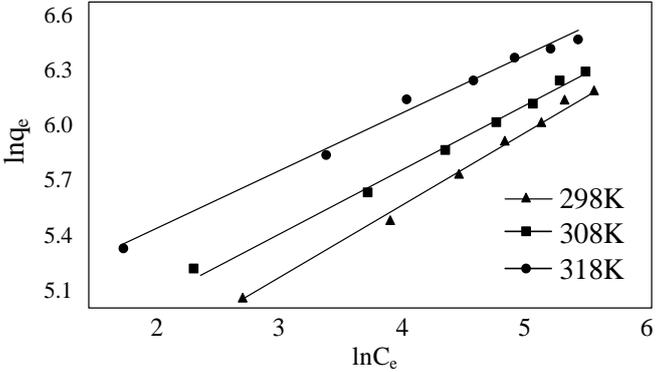


Fig. 6 Adsorption isotherm of ERG5 to TC in Freundlich model

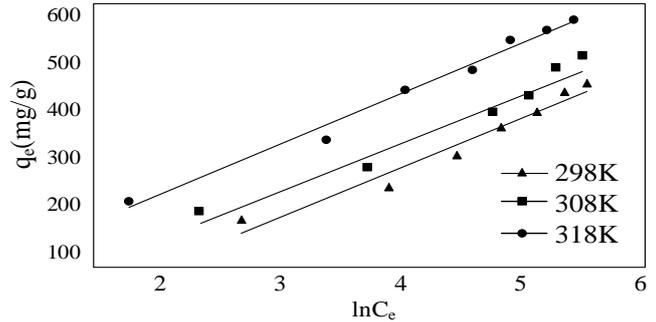


Fig. 7 Isothermal Linear Chart of TC Adsorption by ERG5 in Temkin Model

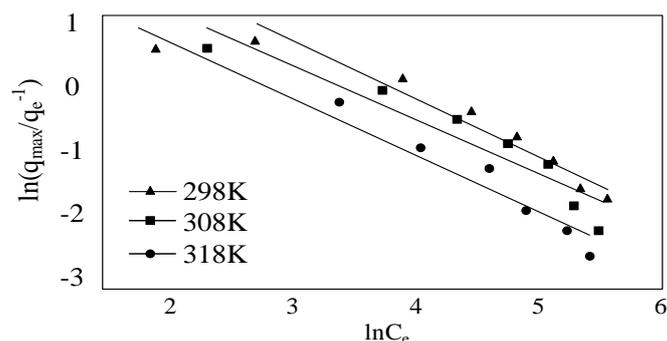


Fig. 8 Isothermal Linear Chart of TC Adsorption by ERG5 in Hill Model

It can be seen from the figure that the Freundlich linear fit coefficient $R^2 \geq 0.99$ at the temperature studied indicates that the Freundlich isothermal model is very suitable for describing the adsorption process of ERG5 to TC, and ERG5 has surface heterogeneity. At the same time, the value of the constant K_F increases with increasing temperature, confirming that the high temperature is favorable for the removal of the adsorbed TC by ERG5. It is known that the adsorption of TC is an advantageous process from a value of $1/n$ between 0 and 1. Regarding the Temkin adsorption isotherm model (see Figure 1.11c), the linear fit coefficient is between 0.95 and 0.98, indicating that the process of TC adsorption to ERG5 can be roughly described. As shown in the figure, the fitting coefficient of the Hill equation is between 0.88 and 0.94, and the synergy coefficient N is less than 1, indicating that there is a negative synergy between the adsorbate TCs. The four water samples used in this experiment were collected from Dasha River, a campus pond, a reservoir and a reservoir in Shenzhen. The sampling points are located in the center of Dasha River, the center of the campus pond, the center of the A reservoir and the center of the B reservoir. The surface water sample (0.5 m from the water surface) is taken by a self-made sampler. The water samples were sent to the laboratory for analysis immediately after collection. The measurement of the three-dimensional fluorescence spectrum was performed on a CARY Eclipse molecular fluorometer (manufactured by Varian, USA), and the water sample was filtered through a 0.45 μm filter to perform three-dimensional fluorescence scanning. The CARY Eclipse molecular fluorometer uses a xenon arc lamp as the excitation source. The excitation wavelength is as high as 200 to 450 nm. The emission scanning wavelength is 300 to 550 nm. The excitation and emission slit width was 10 nm. The excitation wavelength scanning interval was 5 nm. The response time is automatic. The scanning spectroscopy instrument automatically corrects. Data analysis was performed using Cai Eclipse software. The experimental results show that the 3DEEM of the four water bodies have different contour maps and the number of fluorescent peaks, and their peak positions and corresponding fluorescence intensities are also different, as shown in Table 2.

Table 2 Three-dimensional fluorescence peaks of dissolved organic compounds from different sources

Water sample	Fluorescence peak value / nm	Fluorescent peak type	Fluorescence intensity / (a.u.)
Dasha River	$E_x=280, E_m=346$	Class III (proteinoid)	384.36
	$E_x=340, E_m=394$	Class II (Visible acid)	398.95

	$E_x=370, E_m=425$	Class I (Humic acid)	251.14
Campus pond	$E_x=280, E_m=338$	Class III((proteinoid))	196.04
	$E_x=340, E_m=393$	Class II (Visible acid)	156.17
A reservoir	$E_x=340, E_m=392$	Class II (Visible acid)	158.37
	$E_x=370, E_m=423$	Class I (Humic acid)	111.33
B reservoir	$E_x=280, E_m=338$	Class III(proteinoid)	136.70

Same as the reservoir water, the fluorescence peaks in the water bodies of the A reservoir and the B reservoir are completely different: The fluorescence peak of the water in the reservoir is mainly in Class III, which shows strong protein-like fluorescence. The dissolved organic matter in the water is mainly microbial source, and the organic pollution is mainly endogenous pollution. The fluorescence peaks of the water in the B reservoir mainly appear in Class I and Class II, showing humic acid-like fluorescence and fluorite fluorescence in the visible region. The dissolved organic matter in the water is mainly terrestrial humic acid, and its organic pollution is mainly external pollution. The Dasha River water body has three different E_x / E_m -peak positions: Class I、Class II、Class III. It shows that its organic pollution has both endogenous and exogenous pollution. Moreover, its fluorescence intensity is 2.3 to 3.6 times that of reservoir water, and the degree of pollution far exceeds that of reservoir water. It is understood that the organic pollution of the Dasha River mainly comes from various industrial and domestic wastewaters along the upstream and along the way, coupled with small river flow, long hydraulic retention time, and often in the state of stagnant water, thus causing serious endogenous pollution. The fluorescence peaks of the campus pond water appear in Class II and Class III, respectively, and their fluorescence intensity is between the Dasha River water body and the reservoir water body. This indicates that there are both endogenous organic matter and exogenous organic matter in the water body, and the organic matter content is more than the reservoir water and less than the Dasha River water.

5. CONCLUSION

Although it is possible to more intuitively reflect the amount of energy transfer studying the changes in the process with changes in ΔS and ΔS , whether the reaction is thermodynamically feasible also has some shortcomings: A negative value of ΔG is a thermodynamically feasible reaction, but the reaction can not necessarily occur because the reaction is controlled by the activation energy and the intermediate process. When $\Delta G > 0$, the reaction is not possible. The study system is a separator system. When $\Delta S < 0$, it is thermodynamically unfavorable. If it is a non-isolated system, it must be related to the surrounding environment. Even if $\Delta S_{\text{System of matter}} < 0$,

$\Delta S_{\text{Environmental Science}} > 0$, and $\Delta S_{\text{System of matter}} + \Delta S_{\text{Environmental Science}} > 0$, Then the process of change in the system is also a spontaneous process. Three-dimensional fluorescence spectroscopy can obtain complete spectral information of fluorophores in dissolved organic matter. It is a useful spectral fingerprint technique that can be used to analyze and judge the type of organic pollution in water. The experimental results show that the Shenzhen A reservoir is mainly characterized by endogenous pollution; the Shenzhen B reservoir is mainly characterized by external pollution; the Dasha River and the campus pond have both internal and external pollution. The order of organic pollution from high to low is: Dasha River, campus pond, Jia Reservoir, and B Reservoir.

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