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Adsorption and Degradation of Organics in Wastewater on Municipal Sludge

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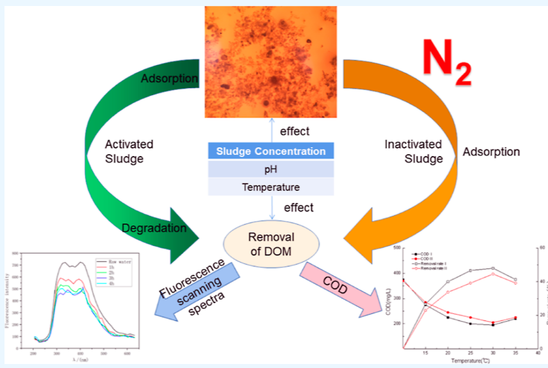
ABSTRACT: Adsorption and degradation of organic compounds on sludge were investigated by comparing activated and inactivated sludge at various dosages, pH values, and temperatures. The organic compounds in wastewater were identified and evaluated through fluorescence spectra. The results show that optimum adsorption occurred as the activated and inactivated sludge concentration was 4000 mg/L at a pH of 7.99 and a temperature of 30 °C. The fluorescence scanning spectrum indicated that activated sludge could remove protein-like organic matter, fulvic acid-like organic matter, and humic acid-like organic matter by 22.1, 9.4, and 41.2%, respectively, via adsorption only or by 25.9, 9.8, and 74.3%, respectively, via adsorption and degradation. Under optimum conditions, by using the good adsorption performance of sludge combined with other sewage treatment technologies, the treatment of high-content organic wastewater can be achieved.



1. INTRODUCTION

Currently, increasing consumption of drinking water generates a large amount of wastewater[1] with the development of the city and intensifies the pressure on the environment. Major pollutants of municipal wastewater come from human excrement, production activities, and waste from animals; and the main components are microorganisms, sugars, oils, proteins, urea, and fats,[2,3] of which 60% are organic matters (suspended matters accounting for more than 75%).[4] Once the pollutant content exceeds the carrying capacity of the water environment, serious environmental problems would arise and threaten human health, ecosystems, and the sustainable development of water resources.[5,6] Adsorption is an important method for pollutant control because of its simple operation and high efficiency.[7] Some sludge could be used as an adsorbent, including activated sludge, anaerobic sludge, nitrified sludge, inactivated sludge, etc.[8] Activated sludge has a large specific surface area and strong adsorption ability, removing pollutants from the wastewater. Recently, the role of activated sludge in the adsorption of organic pollutants has received extensive attention. For instance, Prado et al.[9] found that activated sludge has a good adsorption effect on tetracyclines, and the study of Tang et al.[10] showed that activated sludge has a good adsorption effect on naproxen organic matter. The adsorption of reactive dyes on sludge surfaces is classified as monolayer adsorption. Infrared analysis has revealed that various functional groups on sludge surfaces react with dye molecules, and both primary and secondary sludges are capable of adsorbing a wide range of drugs and perfumes. However, for certain drugs such as diclofenac, the primary sludge has been found to have a lower adsorption capacity than the secondary sludge.[11] The organic matter present in municipal wastewater can be divided into two categories based on particle size (generally 0.45 or 0.22 μm): particular organic matter (POM) and dissolved organic matter (DOM). DOM accounts for 30−40% of the total organic matter and is the primary focus of wastewater treatment.[12] DOM in municipal wastewater is a complex and heterogeneous polymeric organic mixture, comprising humic substances such as humic acid (HA), fulvic acid (FA), amino acids (AA), carbohydrates, surfactants, and so on.[13] Commonly used organic pollutant indicators, such as chemical oxygen demand (COD) and total organic carbon (TOC), can only provide an overall indication of the organic matter content and are unable to accurately reflect the composition and concentration of various dissolved organic substances in wastewater. Fluorescence spectroscopy, however, is better suited to reflect the properties, type, and quantity of organic matter in water due to its high selectivity and sensitivity;[14] fluorescence spectroscopy can be employed for qualitative analysis, quantitative evaluation, and real-time online monitoring of wastewater treatment effects.[15,16] Marhuenda-Egea et al.[17] have demon-

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strated that three-dimensional fluorescence spectroscopy can be utilized to analyze and evaluate soluble organic matter. Xi-Zhi Niu et al.[18] employed three-dimensional fluorescence spectroscopy to investigate the soluble organic matter in black soil. It was observed that an increase in temperature increases the content of HA, while the FA region in the alternately frozen-thawed soil is red-shifted. AluPoaei and García-Rubio[11] discovered that microbes generate numerous fluorescently active compounds, such as enzymes, coenzymes, pigments, and metabolites, which degrade their organic substrates and emit their distinctive fluorescence upon excitation by ultraviolet light.

Activated sludge has been studied as an adsorbent for separating pollutants for 20 years, yet research on the adsorption of municipal wastewater by activated sludge is not comprehensive. Drawing from previous studies, the adsorption performance of activated sludge and inactivated sludge is further discussed from a scientific and practical perspective. Single-factor experiments were conducted to investigate the effects of adsorption time, sludge concentration, pH, and temperature on adsorption performance, and the optimal conditions for adsorption were obtained. The fluorescence characteristics of the water samples treated under different conditions were scanned to analyze the changes in the types and contents of dissolved substances in the water before and after treatment. By exploring the optimum conditions of sludge adsorption, it is possible to improve the adsorption performance of sludge and offers the necessary theoretical basis and reliable scientific foundation for future pollution control technology and practical engineering applications, with important environmental, economic, and social benefits.

2. MATERIALS AND METHODS

2.1. Experimental Materials. The raw water utilized (COD was 300−550 mg/L) was sourced from the grid of the reclaimed water treatment station of Shandong Jianzhu University. To ensure the accuracy of the experiment, the water sample analysis should be completed within 48 h. The wastewater obtained contained numerous large particle suspended matters, thus necessitating filtration with gauze prior to the experiment.

The activated sludge utilized was taken from the mud−water mixture in the aeration tank of the Jinan Water First Water Treatment Plant. It was an aerobic activated sludge with a sludge concentration of approximately 3000 mg/L, exhibiting flocculent, yellowish-brown characteristics, an earthy smell, and a viscous texture. Its zoogloea structure was dense, its shape was irregular, and it contained a wide variety of bacteria, with more than 99% water content and a pH of approximately 7.0. The sludge particles had an uneven surface and a small particle size, resulting in a large specific surface area and adsorption amount. The morphology of activated sludge was observed by 100 times fluorescence microscope (Figure S1).

2.2. Sample Preparation. The activated sludge utilized in the adsorption experiment was directly taken from the biological reaction tank, and the microorganisms present in the sludge had a certain degradation effect on the pollutants in the wastewater, thus making it difficult to accurately determine the adsorption effect of the sludge on the pollutants in the wastewater.[19] Consequently, in this experiment, deactivation of the sludge was achieved through nitrogen blowing, thus reducing the degradation of the target substance by microorganisms. The sludge mixed liquor underwent three successive washes with deionized water, followed by aeration with an air compressor for 6 h in order to supply oxygen. Activated sludge was taken out after aeration, and then nitrogen aeration was conducted for several hours until the dissolved oxygen was 0 mg/L, thus rendering the sludge inactive.[20] The mixed liquor sludge was centrifuged and the supernatant was discarded; the precipitate was washed three times with deionized water and stored in a refrigerator for future use.

2.3. Analysis and Detection Methods. The COD of the wastewater in this experiment was determined by the potassium dichromate method. The wastewater was filtered through a 0.45 μm glass fiber filter and then scanned by a F-4500 fluorescence spectrophotometer (Hitachi, F-4500, Japan), the parameter settings of which are displayed in Table S1. Data analysis was conducted using Origin 9.0 software.

2.4. Fluorescence Characteristics of Activated Sludge Adsorbing Organic Matter in Wastewater. The activated sludge was utilized to adsorb and degrade organic compounds in the wastewater, with the sludge concentration (MLSS) adjusted to 4000 mg/L. Water samples were taken with adsorption times of 1−4 h, and both the raw and adsorbed water samples were filtered through a 0.45 μm microporous membrane to remove insoluble organic compounds. The excitation wavelengths λ_{ex} of the fluorescence spectrophotometer were set to 200, 237, and 340 nm, respectively, and the spectral properties of the water samples were scanned. Subsequently, the fluorescence data of the water samples were fitted using Origin 9.0 software.

2.5. Experiment of Affecting Factors. In the previous study, the adsorption equilibrium experiment was carried out, and the relationship curve between adsorption time and COD concentration was obtained. It is concluded that when the adsorption time reaches 2 h, the adsorption reaches equilibrium. In this study, various influencing factors such as wastewater pH, sludge concentration, and reaction temperature were evaluated in batches. With regard to sludge concentration, an appropriate amount of activated sludge was added at 25 °C and the sludge concentrations were adjusted to 1000, 2000, 3000, 4000 and 5000 mg/L, respectively. For the pH study, the pH of the wastewater was adjusted to 5, 6, 7, 8 and 9 with H_2SO_4 and NaOH, respectively, with the concentration of activated sludge being approximately 4000 mg/L. Lastly, for the temperature study, the adsorption experiments were conducted under the conditions of a water bath temperature of 15, 20, 25, 30, and 35 °C, respectively. The above samples were oscillated at a constant temperature oscillator (Thermo Scientific, 4637-1CECN, USA) at a speed of 130 rpm until adsorption equilibrium was reached. Subsequently, the sample was taken to measure its COD. The supernatant was then filtered through a 0.45 μm microporous membrane, and the spectral properties were scanned by a fluorescence spectrophotometer. Two parallel samples were taken in the experiment, and the measured data were averaged for the result analysis, with a blank experiment being used for comparison. The blank sample is activated sludge in ultrapure water. The measured COD and fluorescence scanning spectra are used as zero references to eliminate the influence of sludge on the experimental data.

The procedure for the inactivated sludge adsorption experiment was largely similar to that of the activated sludge

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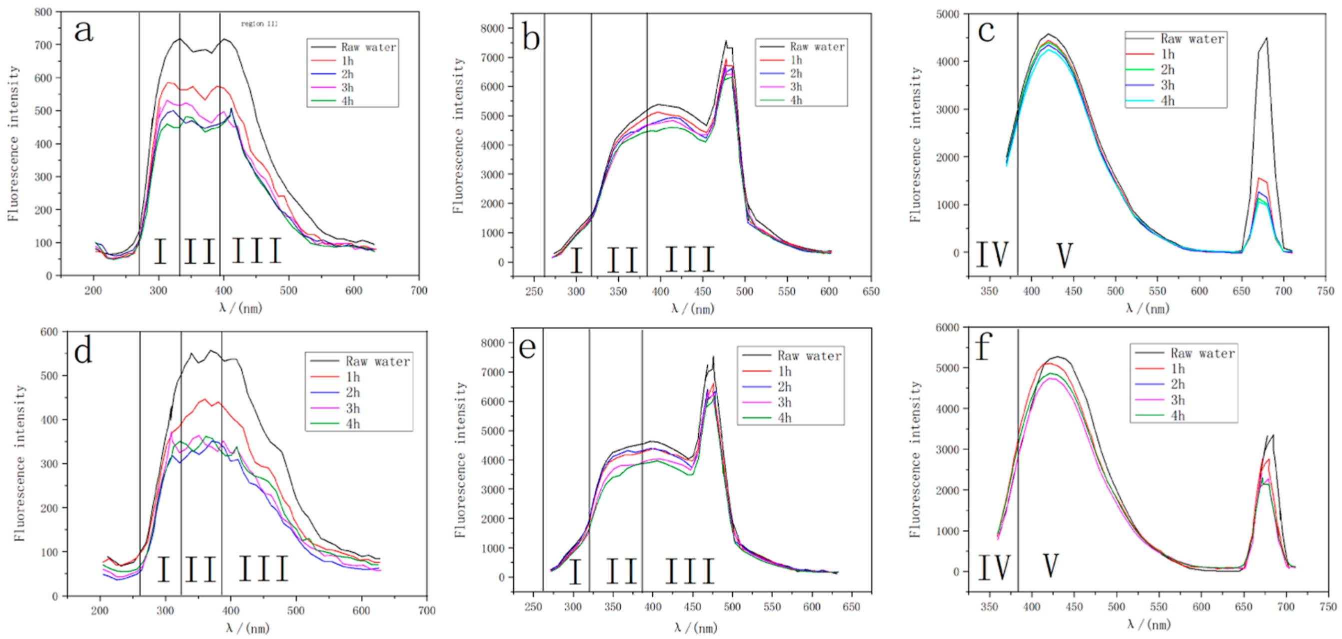

Figure 1. Fluorescence scanning spectra of wastewater before and after adsorption and degradation at excitation wavelength of 200 (a), 237 (b), and 340 nm (c) by activated sludge and at excitation wavelength of 200 (d), 237 (e), and 340 nm (f) by inactivated sludge.

adsorption experiment, the differences are that the wastewater needs to be nitrogen blown in advance to remove dissolved oxygen, and during the entire sterilization sludge experiment, nitrogen blowing conditions were maintained to isolate oxygen and avoid the interference of biodegradation. Upon completion of the adsorption of the inactivated sludge, the water sample treatment method was the same as that of the activated sludge adsorption experiment.

3. RESULTS AND DISCUSSION

3.1. Fluorescence Characteristics of Organic Compounds in Wastewater Adsorbed by Sludge. *3.1.1. Activated Sludge.* Coble et al.[21,22] showed that the peak of EEM was related to tyrosine-like, phenol-like, humic-like, or tryptophan-like organic matter. Chen et al.[23] divided the fluorescence peak position of different kinds of DOM in water into five regions according to the position of excitation (Ex) and emission (Em) wavelengths. According to Chen et al.'s conclusion and this experiment, Regions I and II can be defined as having shorter excitation and emission wavelengths ($\lambda_{ex}/\lambda_{em}$ = (200−250) nm/(200−380) nm) and involve amino acids with aromatic R groups such as tryptophan, tyrosine and phenylalanine, which are the fluorescent regions of easily degradable organic compounds The region related to fulvic acid-like organic matter is Region III, which has a shorter excitation wavelength and a longer emission wavelength ($\lambda_{ex}/\lambda_{em}$ = (200−250) nm/(>380 nm)), contains fulvic acid-like organic matter, and is the fluorescent region of the degradable complex mixture of compounds. When the excitation wavelength and emission wavelength are both longer (($\lambda_{ex}/\lambda_{em}$ = (250−450) nm/(260−380) nm), it represents Region V, which is a refractory organic fluorescent region related to humic acid-like organic matter organics.[24,25] Yang et al.[26] have demonstrated that the fluorescence parameters exhibit a strong linear correlation with COD, indicating that the fluorescence parameters are suitable for characterizing the content of DOM in wastewater.

Fluorescence spectrum scanning was performed after using activated sludge to treat wastewater at different times. Three excitation wavelengths were selected. Both 200 and 237 nm belong to the category of shorter excitation wavelengths, and one is the critical value and the other is the intermediate value, which is the typical representative. The excitation wavelength of 340 nm belongs to the category of longer excitation wavelengths, and the three excitation wavelengths selected have the best peak effect. However, there are some limitations in selecting only three excitation wavelengths, which may not fully reflect each substance. Further research will carry out more excitation wavelength experiments to make up for this shortcoming. When $\lambda_{ex}/\lambda_{em}$ = 200 nm/(320 ∼ 420) nm, one fluorescence peak was observed (Figure 1a), corresponding to the presence of protein-like organic matter. A fluorescence peak (Figure 1b) was observed at $\lambda_{ex}/\lambda_{em}$ = 237 nm/(380−480) nm, corresponding to the presence of fulvic acid-like organic matter. It is likely that the presence of two strong fluorescence peaks was due to the different functional groups present in the fulvic acid-like organic matter, which resulted in different fluorescence characteristics.[27] When the excitation wavelength was 340 nm (Figure 1c), a fluorescence peak appeared at the emission wavelength of 420−680 nm, corresponding to the organic compound humic acid-like organic matter. The fluorescence intensity of the protein-like organic matter, fulvic acid-like organic matter, and humic acid-like organic matter decreased by 18.5, 6.34, and 69.9%, respectively, at 1 h of adsorption, indicating that the content of these three organic compounds and complex mixture of compounds in wastewater decreased rapidly and significantly, belonging to the fast adsorption stage. After 2 h of reaction, the fluorescence intensity reductions of protein-like organic matter, fulvic acid-like organic matter, and humic acid-like organic matter were 25.9, 9.8, and 74.3%, respectively. Subsequently, with the increase of adsorption time, the fluorescence intensity no longer decreased, indicating that the adsorption had reached equilibrium. In conclusion, the activated sludge can effectively adsorb the protein-like organic matter, fulvic acid-

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like organic matter, and humic acid-like organic matter in the wastewater.

3.1.2. Inactivated Sludge. Fluorescence spectrum scanning was performed after using inactivated sludge to treat wastewater at different times. When the excitation wavelength was 200 nm (Figure 1d), a fluorescence peak appeared at the emission wavelength of 320−420 nm, corresponding to the organic compound protein-like organic matter. At 237 nm (Figure 1e), a peak at 380−480 nm was observed, which was attributed to fulvic acid-like organic matter. When the excitation wavelength was 340 nm (Figure 1f), a fluorescence peak appeared at the emission wavelength of 420−680 nm, corresponding to humic acid-like organic matter. Two strong fluorescence peaks were observed near the wavelengths of λ_{em} = 420/670 nm. The fluorescence intensity of the protein-like organic matter, fulvic acid-like organic matter, and humic acid-like organic matter decreased by 20.7, 8.81, and 19.2%, respectively, after 1 h of adsorption, indicating a significant decrease in the content of the three organic compounds in the wastewater. After 2 h, the fluorescence intensity reductions of the protein-like organic matter, fulvic acid-like organic matter, and humic acid-like organic matter were 28.8, 11.8, and 30.8%, respectively. Subsequently, the fluorescence intensity decreased insignificantly, suggesting that the adsorption had reached equilibrium. In conclusion, it can be observed that inactivated sludge is capable of effectively adsorbing the protein-like organic matter, fulvic acid-like organic matter, and humic acid-like organic matter present in the wastewater.

3.2. Effect of Sludge Concentration on Sludge Adsorption and Degradation. The removal effect of COD in wastewater under different sludge concentrations is illustrated in Figure 2. When the concentration of activated sludge and inactivated sludge increased from 1000 to 4000 mg/L, the adsorption rate of COD increased by 27.5 and 25.2%, respectively, which may be attributed to the increase of adsorption sites caused by the increase of sludge concentration. This conjecture is in agreement with the research findings of Bazrafshan et al.[28] and Feng et al.,[29] who demonstrated that the increase of sludge concentration not only increases the adsorption surface area but also increases the number of functional groups involved in adsorption, thus increasing the number of adsorption sites. When the concentration of the two sludges was 5000 mg/L, the removal rate of COD was no longer changed, which may be related to the saturation of adsorption sites. The study of Wei and Zhang et al.[30] corroborates this point, wherein the sludge is too crowded to effectively cover some adsorption sites, thus preventing organic compounds from binding to the active sites, resulting in a decrease in adsorption capacity. Consequently, if the sludge concentration is blindly increased, not only will the removal efficiency of COD not be improved, but also sludge will be wasted. The experimental results demonstrate that the adsorption effects of the two kinds of sludge on organic compounds are essentially the same. When the sludge concentration was 4000 mg/L, the COD removal effect was optimal. Subsequently, with the increase of sludge concentration, the removal rate did not change significantly. Therefore, the optimum concentration of activated sludge was determined to be 4000 mg/L.

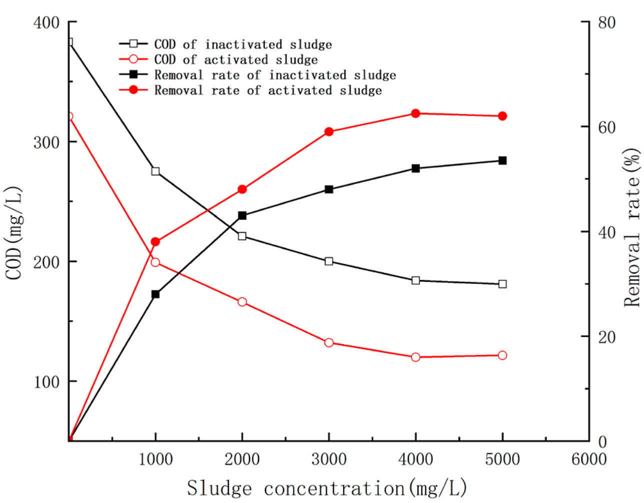

Figure 2. Effect of sludge concentration on sludge adsorption.

3.2.1. Effect of Sludge Concentration on Fluorescence Characteristics of Organic Compounds Adsorbed by Activated Sludge. Wastewater was treated with different concentrations of activated sludge, and three-dimensional fluorescence spectrum scanning was performed. Since the experiment focused on the effect of sludge adsorption, the subsequent study of activated sludge did not fully use the three excitation wavelengths for spectral scanning. At an excitation wavelength of 200 nm (Figure 3a), a fluorescence peak was observed at an emission wavelength of 300−500 nm, with a peak height of 352, corresponding to the organic compound protein-like organic matter. After adsorption of different concentrations of sludge, the fluorescence peak height decreased to 266−223. A fluorescence peak at the excitation wavelength of 237 nm and the emission wavelength of 380−500 nm corresponds to a complex mixture of fulvic acid-like organic matter compounds (Figure 3b). After adsorption, the fluorescence peak gradually decreased from 6335 to 5326. This indicates that the adsorption amount of protein-like organic matter and fulvic acid-like organic matter increases with the increase of activated sludge concentration. When the sludge concentration reached 5000 mg/L, the fluorescence peaks did not decrease at the two excitation wavelengths. Thus, it is suggested that the optimal sludge concentration for adsorption of protein-like organic matter and fulvic acid-like organic matter in wastewater is 4000 mg/L.

3.2.2. Effect of Sludge Concentration on Fluorescence Characteristics of Organic Compounds Adsorbed by Inactivated Sludge. Wastewater was treated with different concentrations of inactivated sludge, and three-dimensional fluorescence spectrum scanning was performed. At an excitation wavelength of 200 nm (Figure 3c), a fluorescence peak with a peak height of 568 was detected at an emission wavelength of 300−500 nm, which was associated with the presence of proteinoid. Following the adsorption of different concentrations of sludge, the fluorescence peak height decreased to 482.5−399. A fluorescence peak of fulvic acid-like organic matter was observed at an excitation wavelength of 237 nm and an emission wavelength of 380−500 nm (Figure 3d). With the adsorption process, the fluorescence peak gradually decreased from 7869 to 6546. When the excitation wavelength was 340 nm (Figure 3e), two fluorescence peaks were observed at 420 nm and 670 nm, with peak heights of 4239 and 4247, respectively. This was attributed to humic acid-like organic matter. Following the adsorption process, the fluorescence peak gradually decreased to 1317. The results

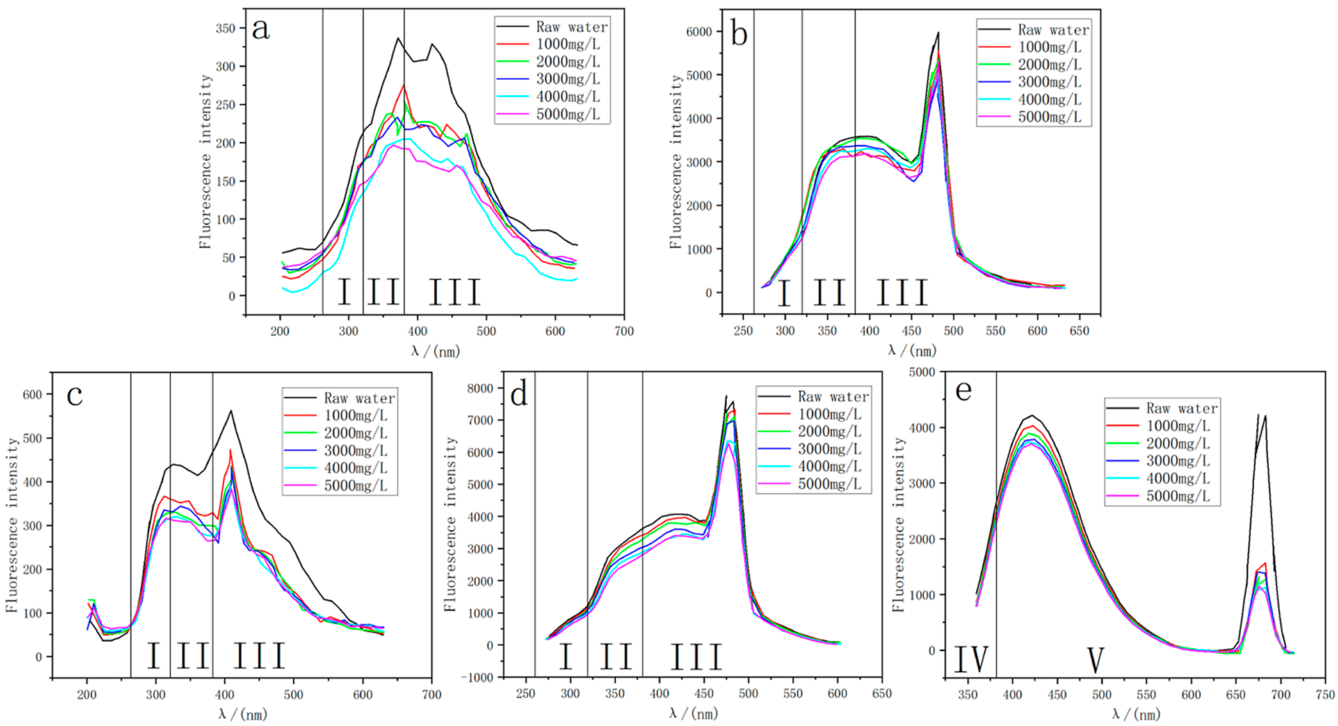

Figure 3. Fluorescence scanning spectra of wastewater before and after adsorption and degradation at excitation wavelengths of 200 (a) and 237 nm (b) by activated sludge, and at excitation wavelength of 200 (c), 237 (d), and 340 nm (e) by inactivated sludge.

indicate that the adsorption amount of protein-like organic matter, fulvic acid-like organic matter, and humic acid-like organic matter increases with the increase of the inactivated sludge concentration. When the sludge concentration reached 5000 mg/L, the fluorescence peaks did not decrease at the two excitation wavelengths. Consequently, it is more suitable to adsorb the protein-like organic matter and fulvic acid-like organic matter in the wastewater when the sludge concentration is 4000 mg/L.

3.3. Effect of pH on Sludge Adsorption and Degradation. The results of the adsorption are depicted in Figure 4. As the pH increased, the COD of the wastewater gradually decreased when the adsorption of activated sludge and inactivated sludge reached equilibrium. When the pH was 7.99, activated sludge and inactivated sludge had the highest adsorption capacity of COD, and the COD removal rates were 45.9 and 44.3%, respectively. Different from the conclusion of Hamon et al.,[20] the removal rate of COD in their experiment was 0% after 2 h of adsorption, which may be related to the fact that glucose was the only COD in their experiment. Sludge adsorption may fail to adsorb glucose-containing substances. The COD in this study is an extremely complex mixture. The sludge has an obvious adsorption effect on humus and protein-like organic matter, which may lead to the decrease of COD in the inactivated sludge experiment. In addition, the adsorption of organic matter by sludge has a physical adsorption effect,[31] so the reduction of COD should occur. As indicated in Table 1, when the two sludges were adsorbed in an acidic environment (pH 5 to 6), the pH of the wastewater rose after the adsorption was completed. Conversely, in the neutral and alkaline environments, the pH of wastewater tended to remain stable after adsorption. This was because in an acidic environment, the H^+ in the water occupied the adsorption site, thus hindering the binding of activated sludge to organic compounds. When the adsorption site was occupied by H^+, the concentration of H^+ in water decreased, resulting in an increase in the pH of the wastewater. This demonstrates that the adsorption effect of sludge is more effective than that of the acidic environment when the wastewater is in a neutral or alkaline environment.[32] This further confirms the accuracy of the conclusion that the sludge has the most optimal adsorption effect when the wastewater pH is 7.99.

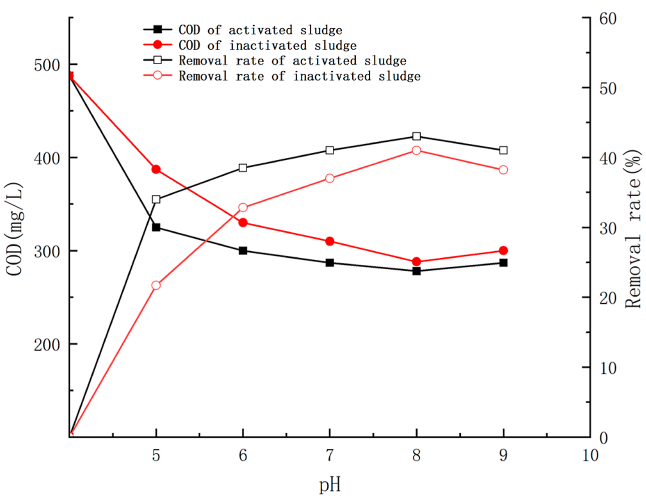

Figure 4. Effect of pH on sludge adsorption.

Table 1. Comparison of pH Changes of Sewage before and after Sludge Adsorption

before adsorption	5.00	6.03	7.02	7.98	8.99
after adsorption and degradation	5.81	6.68	7.29	7.82	8.83
after simple adsorption	5.95	6.71	7.46	7.97	8.78

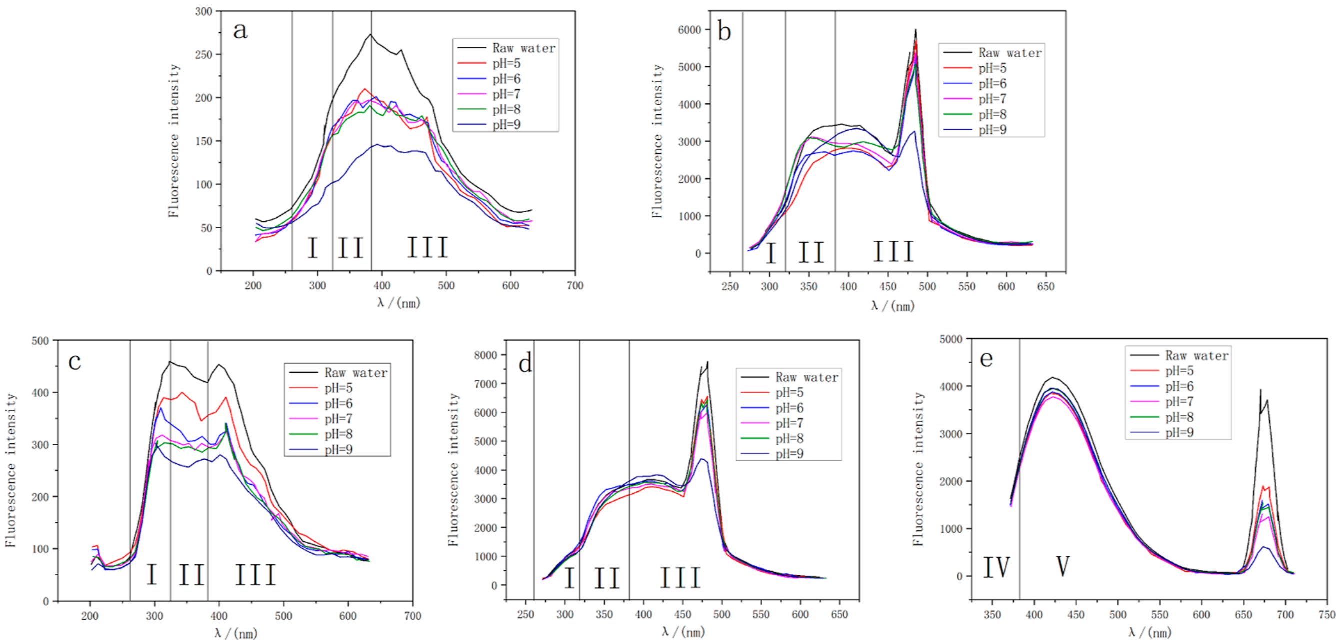

Figure 5. Fluorescence scanning spectra of wastewater before and after adsorption and degradation at excitation wavelength of 200 (a) and 237 nm (b) by activated sludge and at excitation wavelengths of 200 (c), 237 (d), and 340 nm (e) by inactivated sludge.

3.3.1. Effect of pH on Fluorescence Characteristics of Organic Compounds Adsorbed by Activated Sludge. The adsorption and degradation experiments of activated sludge at different pHs were carried out, and fluorescence spectrum scanning was used. When the excitation wavelength was 200 nm (Figure 5a), one fluorescence peak appeared at the emission wavelength of 300−500 nm, with the fluorescence peak at 278, corresponding to the organic compound protein-like organic matter. After the adsorption at pH 5 to 8, the decrease in fluorescence intensities of the wastewater was essentially the same, indicating that protein-like organic matter adsorbed by activated sludge was not affected by the pH in this range. When the pH was 9, the fluorescence peak decreased by 137 compared to that of the raw water. Analysis of the pH value of the sludge revealed that it had a good adsorption effect on proteins when the pH value was 9. When λ_{ex} = 237 nm, λ_{em} = (380−550) nm, two fluorescence peaks were observed (Figure 5b), with the corresponding complex mixture of compounds being fulvic acid-like organic matter. The two fluorescence peaks at $\lambda_{ex}/\lambda_{em}$ = 237/(380−550) nm were significantly reduced after adsorption at pH 5 to 8, with a decrease of 1020 and 800, respectively, compared to the raw water. The adsorption effect of the sludge on fulvic acid-like organic matter was not affected by pH within this range. However, after adsorption at pH 9, the fluorescence peak at $\lambda_{ex}/\lambda_{em}$ = 237/(440−550) nm decreased by 3000, indicating that the activated sludge had the best adsorption effect on acid at pH 9.

3.3.2. Effect of pH on Fluorescence Characteristics of Organic Compounds Adsorbed by Inactivated Sludge. The adsorption and degradation experiments of inactivated sludge at different pH were carried out, and the fluorescence spectrum scanning was used. A protein-like organic matter fluorescence peak appeared (Figure 5c) at the excitation wavelength of 200 nm and the emission wavelength of 300−500 nm, and the peak intensity is 468. This was attributed to the presence of protein-like organic matter. After adsorption at pH 5−9, the fluorescence intensity of the wastewater decreased with increasing pH, with the greatest decrease (157) observed at pH 9. At an excitation wavelength of 237 nm (Figure 5d), a fluorescence peak appeared at an emission wavelength of 440−500 nm, with a peak intensity of 7737. This was attributed to the presence of fulvic acid-like organic matter. After adsorption at pH 5−8, the decrease in fluorescence intensity of the wastewater was similar, indicating that fulvic acid-like organic matter adsorption by inactivated sludge was not affected by pH in this range. At pH 9, the fluorescence intensity decreased by 3344. When excited at a wavelength of 340 nm (Figure 5e), two fluorescence peaks with peak intensities of 4204 and 3894 were observed at an emission wavelength of 400−700 nm. This was attributed to the presence of humic acid. After adsorption at pH 5−8, the two fluorescence peaks decreased by 2335, indicating that humic acid adsorption by inactivated sludge was not affected by pH in this range. At pH 9, the fluorescence peak at $\lambda_{ex}/\lambda_{em}$ = 237/(440−550) nm was most significantly reduced, with a decrease of 3274.9. Overall, the optimal pH for the adsorption of organic compounds in wastewater by inactivated sludge appeared to be 9.

3.4. Effect of Temperature on Sludge Adsorption and Degradation. Between 15 and 30 °C, an increase in temperature was observed to result in a gradual decrease of the COD of the wastewater adsorption equilibrium point (Figure 6). When the temperature reached 30 °C, the adsorption capacity of COD by activated sludge and inactivated sludge were found to be the highest, with respective COD removal rates of 51.6 and 48.4%. In comparison, the COD adsorption capacity of sludge at 15 °C was significantly lower than that at 20, 25, and 30 °C, indicating that low temperatures are not conducive to the adsorption reaction. As the temperature of the system increased to 35 °C, the removal rate of COD adsorbed by the two sludges decreased to 40.4 and 38.3%, respectively, likely due to mass transfer resistance in the adsorption reaction of sludge and organic compounds. This is thought to be due to the decreased thickness, viscosity,

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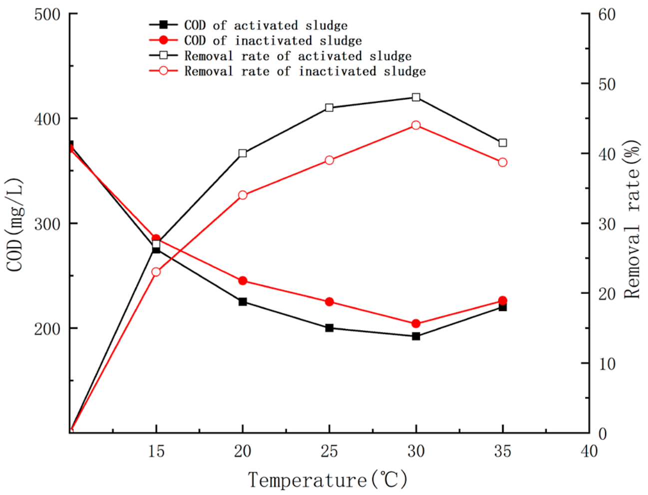

Figure 6. Effect of temperature on sludge adsorption.

and density of the interface solution films, which in turn increases the speed of ion diffusion and activates numerous adsorption sites.[33] Therefore, an appropriate rise in temperature is advantageous to augment the adsorption efficiency; however, excessively high temperatures may have an adverse effect. Wang et al.[34] also proposed the same perspective: when the temperature is too high, the speed of ion diffusion is increased, resulting in a decrease in the stability of the equilibrium point of the reaction. This, in turn, leads to the release of organic compounds that are bound firmly to the surface of the sludge into the water, thus reducing the sludge's adsorption efficiency. Consequently, it can be concluded that the sludge has the highest adsorption effect on organic matter at 30 °C, whereas temperatures that are too high or too low are not conducive to the adsorption of organic compounds by the sludge. This is in agreement with the findings of Rudolfs et al.[35]

3.4.1. Effect of Temperature on Fluorescence Characteristics of Organic Compounds Adsorbed by Activated Sludge. The wastewater was treated by activated sludge at different temperatures and scanned by fluorescence spectroscopy. At an excitation wavelength of 200 nm (Figure 7a), a single fluorescence peak at an emission wavelength of 300−500 nm (with a peak value of 165.8) was observed, corresponding to a protein-like organic matter compound. Upon adsorption at temperatures ranging from 15−30 °C, a decrease in the fluorescence intensity of the wastewater of 76.9 was observed. At an excitation wavelength of 237 nm (Figure 7b), two fluorescence peaks at an emission wavelength of 380−500 nm (with peak values of 3845 and 6348, respectively) were observed, corresponding to fulvic acid-like organic matter. Upon adsorption at temperatures ranging from 15 to 30 °C, the fluorescence intensities of the wastewater decreased to 3141 and 5465, respectively. At an excitation wavelength of 340 nm (Figure 7c), two fluorescence peaks at an emission wavelength of 380−700 nm (with peak values of 4989 and 3226, respectively) were observed, corresponding to a humic-like acid. Upon adsorption at temperatures ranging from 15 to 30 °C, the fluorescence intensities of the wastewater decreased to 4476 and 1829, respectively. At excitation wavelengths of 200, 237, and 340 nm, an increase in the fluorescence intensity of the wastewater was observed at 35 °C as compared to that at 30 °C. In conclusion, activated sludge has a better adsorption effect on protein-like organic matter, fulvic acid-like organic matter, and humic-like acid compounds at a temperature of 30 °C.

3.4.2. Effect of Temperature on Fluorescence Characteristics of Organic Compounds Adsorbed by Inactivated Sludge. The wastewater was treated by inactivated sludge at different temperatures and scanned by fluorescence spectroscopy. At an excitation wavelength of 200 nm (Figure 7d), the fluorescence peak was observed at an emission wavelength of 300 to 500 nm, with a value of 203.5, corresponding to a

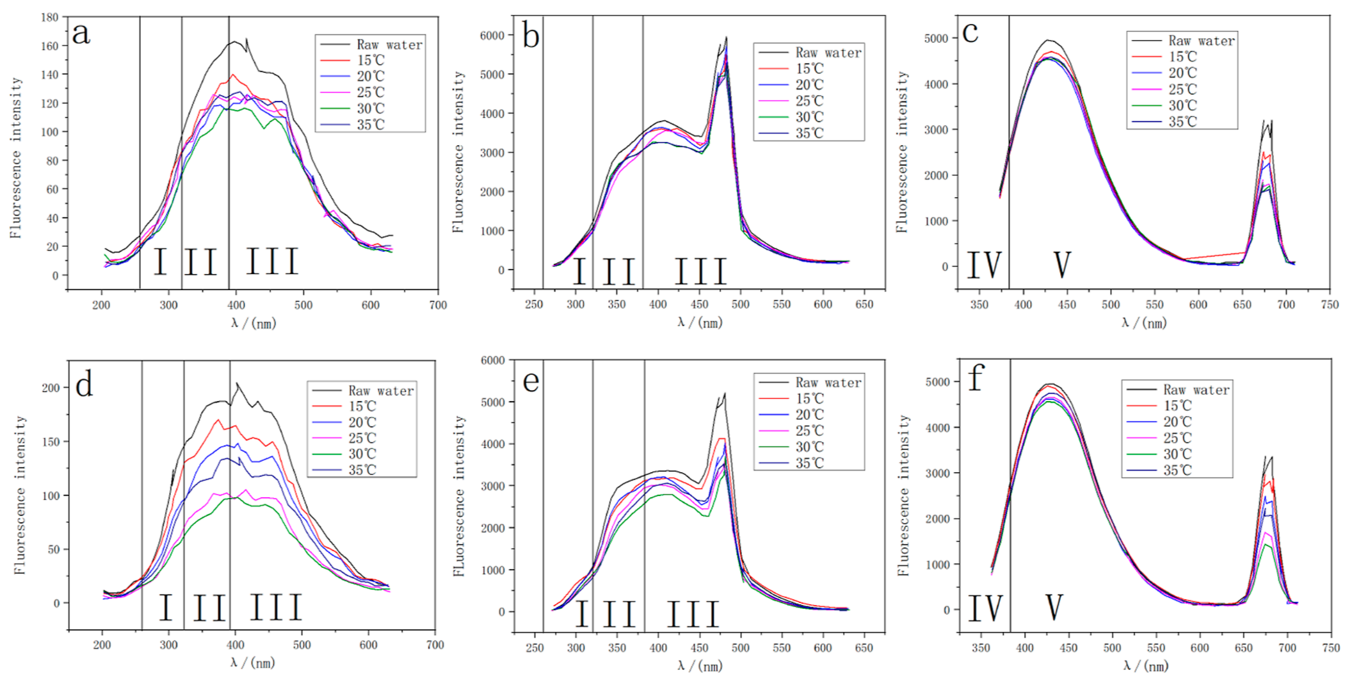

Figure 7. Fluorescence scanning spectra of wastewater before and after adsorption and degradation at excitation wavelength of 200 (a), 237 (b), and 340 nm (c) by activated sludge and at excitation wavelength of 200 (d), 237 (e), and 340 nm (f) by inactivated sludge.

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protein-like organic compound. After adsorption at temperatures of 15 to 30 °C, the fluorescence intensity of the wastewater decreased by 154.9. Upon excitation at 237 nm (Figure 7e), two fluorescence peaks were detected at an emission wavelength of 380−500 nm, with peak values of 3386 and 5207, respectively, indicating the presence of fulvic-like acid. Following adsorption at temperatures ranging from 15 to 30 °C, the fluorescence intensities of the wastewater were reduced to 3141 and 5465, respectively. At an excitation wavelength of 340 nm (Figure 7f), two fluorescence peaks were observed at an emission wavelength of 380 to 700 nm, with values of 4915 and 3304, respectively, corresponding to humic acid-like organic matter. Through adsorption at 15 to 30 °C, the fluorescence intensities of the wastewater decreased to 4565 and 1385, respectively. Under excitation wavelengths of 200, 237, and 340 nm, the fluorescence intensity of wastewater at 35 °C was slightly higher than that at 30 °C. In conclusion, when the temperature was 30 °C, the inactivated sludge had a better adsorption effect on protein-like organic matter, fulvic acid-like organic matter, and humic acid-like organic matter.

4. CONCLUSIONS

In this study, the adsorption properties of activated sludge and inactivated sludge for organic compounds and organic complex mixtures of compounds in wastewater were investigated. The main conclusions are as follows:

1 With the increase of sludge concentration, pH, and temperature, the adsorption and degradation of organic compounds and organic complex mixtures of compounds by activated sludge and inactivated sludge will increase. When the sludge concentration is 4000 mg/L at a pH of 7.99 and a temperature of 30 °C, both activated sludge and inactivated sludge have a better effect on the removal of COD from wastewater.

2 According to the fluorescence scanning spectrum, activated sludge and inactivated sludge can effectively adsorb and remove the protein-like organic matter, fulvic acid-like organic matter, and humic acid-like organic matter in wastewater.

3 According to the fluorescence scanning spectrum, it is more suitable to adsorb the protein-like organic matter and fulvic acid-like organic matter in wastewater when the sludge concentration is 4000 mg/L at a pH of 9 and the temperature of 30 °C.

4 Activated sludge has good adsorption performance for organic matter. Therefore, activated sludge can be used as an adsorbent, combined with other technologies, to treat wastewater with high organic matter content under optimal conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c02765.

Parameter setting of the F-4500 fluorescence spectrophotometer and optical microscopy of activated sludge (PDF)

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Notes

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