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Research Paper

Study on the Removal of Trace Organic Matter from Water by the Ozone-Activated Carbon (O_3-C) Process

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Abstract. The Ozone-Activated Carbon (O_3-AC) process leverages the synergistic action of ozone oxidation and activated carbon adsorption to eliminate trace organic compounds from water, establishing itself as one of the most prevalent integrated technologies in advanced water treatment. In conventional O_3-AC systems, the activated carbon filter bed accumulates significant dissolved oxygen from ozone decomposition, along with adsorbed and concentrated organic constituents. Therefore, after a period of operation, a large number of microorganisms inevitably grow on the activated carbon surface, causing the activated carbon, which primarily functioned by adsorption, to eventually transform into biological activated carbon, and its adsorption capacity rapidly declines. To address these issues, this study combines ozone and activated carbon within the same reactor, forming an integrated Ozone-Activated Carbon (O_3/C) process. Through the contact oxidation effect of ozone on the activated carbon, it aims to maintain the adsorption capacity of the activated carbon on one hand, and achieve synchronous regeneration of the activated carbon on the other. This study used three organic compounds with different solubilities and biodegradabilities in water—phenol, Rhodamine B (RhB), and humic acid—as representative pollutants to investigate the removal efficiency of two different ozone-activated carbon combination processes for these three pollutants. The stability of the effluent quality under impacts such as changes in raw water concentration, before and after backwashing, and ozone interruption was observed. Finally, characterization techniques including Scanning Electron Microscopy (SEM), Brunauer–Emmett–Teller (BET) surface area and porosity analysis, and Fourier Transform Infrared Spectroscopy (FT-IR) were employed to examine alterations in the surface morphology of activated carbon following prolonged operation. These methods were used to assess the effect of ozone on the activated carbon structure and to investigate the operational mechanisms underlying ozone-activated carbon catalytic oxidation and the simultaneous ozone-mediated regeneration of activated carbon. Through comparative analysis of the operational results of the two processes, it was concluded that the effluent removal effects of phenol and RhB by the O_3/C process were superior to those of the O_3-C process, while the removal effects of humic acid, turbidity, ammonia nitrogen, and CODMnwere similar between the two processes. When the influent phenol concentration fluctuated and the influent pollutants were switched multiple times, the O_3/C process recovered stability more rapidly, indicating that the O_3/C process has better adaptability to changes in raw water pollutant types and more stable treatment performance. After backwashing the activated carbon layer, both combined processes could restore their average treatment efficiency to the pre-backwashing level. In the case of ozone interruption in the process, the O_3/C process maintained stability for a longer duration, indicating that the O_3/C process has good buffering capacity during treatment.

Keywords: *Integrated Ozone Activated Carbon Process; Ozone-Biological Activated Carbon Process; Synchronous Adsorption Regeneration*

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1 Introduction

With the accelerating pace of urbanization and industrialization, harmful substances in water bodies continue to increase, and source water pollution is gradually becoming more severe. The direct or indirect discharge of human production and domestic sewage into natural water bodies causes changes in water quality of rivers, lakes, oceans, groundwater, etc., leading to deteriorating source water quality and reducing the utility value of water bodies. This phenomenon is called water pollution [1]. Generally, although the concentrations of organic matter, ammonia nitrogen, phosphorus, etc., in slightly polluted source water are relatively low, the variety of pollutants is numerous, water quality is complex, affecting water's secondary use. The main causes of micro-pollution in drinking water sources are the ineffective treatment of sewage from industrial production, agricultural activities, and leachate from domestic waste before direct discharge into natural water bodies [2]. Although the sources of micropollutants in micro-polluted source water vary from region to region, the components of micropollutants are mainly natural organic matter from biological metabolism, synthetic organic compounds (such as emerging pollutants and pesticides), and ammonia nitrogen [3]. Among them, most synthetic organic compounds are characterized by being difficult to degrade, toxic, and having teratogenic, mutagenic, and carcinogenic effects [4]. Therefore, micro-polluted source water poses potential hazards to human health, and conventional treatment processes in water treatment plants often struggle to remove them effectively, necessitating the development of new, efficient advanced treatment technologies.

Advanced oxidation technologies for micro-polluted source water often use highly oxidizing substances such as potassium permanganate, sodium hypochlorite, and ozone to decompose and remove trace organic matter in water through oxidation [5]. When potassium permanganate is used for oxidation treatment, it can effectively control the formation of chlorophenols and trihalomethane precursors in water, has good removal effects on organic matter, color, odor, taste, and other water quality indicators, and also has high removal capacity for olefins, aldehydes, and ketones. Furthermore, the nascent hydrated manganese dioxide formed by potassium permanganate can adsorb algae in water, increase the settling velocity of algae, and promote algae removal [6]. Research data found that the CODMnremoval rate of effluent after potassium permanganate pre-oxidation can reach 72% [7], and the UV254removal rate can reach 38.2% [8]. However, the oxidation process of potassium permanganate sometimes produces mutagenic intermediate products that are not easily removed by subsequent processes, requiring further effective removal by follow-up treatment. Ozone (O_3) is also one of the most widely used pre-oxidants in water treatment today. Its powerful oxidation performance can decompose dissolved organic matter in water bodies, remove odor substances, reduce disinfection by-product precursors, improve the biodegradability of organic matter, enhance coagulation efficiency, reduce coagulant dosage, and thereby improve treatment efficiency, ensure effluent quality. The removal rate of ammonia nitrogen by ozone oxidation is generally around 40% [9], but the removal efficiency for organic matter indicators, such as TOC and CODMn, is often not high. This is because ozone oxidation cannot completely oxidize and decompose trace organic matter in water; it generally only breaks down high molecular weight organic matter containing benzene rings into low molecular weight organic matter without benzene rings, or oxidizes organic matter with high electron density unsaturated bonds into saturated bond-containing organic matter, resulting in little change in the total organic carbon content in water after oxidation. O_3 can decompose organic matter containing nitrogen groups, releasing ammonia nitrogen, leading to an increase in ammonia nitrogen content in the ozone oxidation effluent [10]. Therefore, standalone ozone pre-oxidation often has certain shortcomings. In practical applications, ozone is usually combined with activated carbon.

Activated carbon adsorption technology exploits the large specific surface area and well-developed pore structure of activated carbon to adsorb organic substances from water. Presently, activated carbon adsorption stands as one of the most effective water treatment methods for eliminating odor, taste, color, chlorinated organics, pesticides, and synthetic organic compounds from drinking water [11]. Activated carbon can be applied independently, utilizing its strong adsorptive capacity to remove organic pollutants and thereby improve water quality. However, due to the saturation issue of activated carbon adsorption capacity, activated carbon is often combined with other methods in practical applications to achieve better results. The Ozone-Activated Carbon (O_3-AC) integrated process is the most widely adopted combined treatment configuration. It effectively merges the oxidative capability of ozone with the adsorptive function of activated carbon to achieve highly efficient removal of trace organic pollutants from water. In the O_3-AC system, ozone oxidizes recalcitrant, high-molecular-weight organic compounds into smaller organic molecules, altering their molecular structures. The resulting

oxidation byproducts are then adsorbed and removed by the activated carbon, thereby accomplishing the overall objective of pollutant elimination. Research data show [6] that activated carbon adsorption technology can achieve removal rates of 80%, 70%, and 95% for CODMn, UV254, and trichloromethane, respectively, indicating that activated carbon adsorption has good removal effects on micro-polluted source water.

The Ozone-Activated Carbon (O_3-AC) process is the most extensively employed advanced treatment technology in water supply systems. This process combination separates ozone oxidation and activated carbon filtration into two independent units. However, in practical application, due to insufficient oxidation capacity of standalone ozone and low efficiency of direct contact reaction between ozone and water, the oxidation effect of ozone on structurally complex organic matter in micro-polluted source water is affected. On the other hand, in the subsequent activated carbon unit, the growth of a large number of microorganisms on the activated carbon surface leads to a rapid decline in the adsorption performance of the activated carbon. Meanwhile, the biodegradation capacity is affected by various factors such as organic matter type, microorganism type, and contact time, resulting in poor removal effects on some refractory organic matter. Therefore, for the above reasons, the existing combined ozone and activated carbon process has technical shortcomings in the treatment of micro-polluted source water. Targeting these issues, this project innovatively combines ozone and activated carbon to form a new integrated Ozone-Activated Carbon process. The aim is to synchronize the reactions of ozone, activated carbon, and trace organic matter in water within the same reactor, organically combining the catalytic decomposition of ozone by activated carbon, the adsorption enrichment and reaction acceleration on the activated carbon surface, and the synchronous regeneration of activated carbon adsorption sites by ozone, to achieve the following three process objectives: first, use ozone to inhibit microbial growth and continuously maintain the adsorption capacity of activated carbon; second, promote the conversion efficiency of ozone into more highly oxidizing •OH radicals, improving the oxidation effect of ozone on complex micro-pollutants; third, strengthen the dynamic regeneration effect of ozone on activated carbon adsorption active sites, extending the service life of activated carbon.

This study constructed a new integrated Ozone-Activated Carbon combined process (O_3/C) and compared it with the traditional Ozone-Biological Activated Carbon combined process (O_3-C) for the removal of three representative micro-pollutants. The removal rates and process stability of the two processes were evaluated through long-term operation, and the operational parameters of the integrated combined process were analyzed. This study aims to refine the integration method of ozone and activated carbon, enhancing the treatment efficacy of the Ozone-Activated Carbon (O_3-AC) process for micro-polluted source waters. The study has important guiding significance for developing new Ozone-Activated Carbon processes and optimizing their operation.

2 Experimental Process

2.1 Wastewater Preparation

The phenol solution used in the experiment was prepared using pure water as a stock solution. The prepared phenol stock solution had a mass concentration of 5000 mg/L. Accurately weigh 5g of phenol using an analytical balance, transfer the dissolved phenol solution to a volumetric flask, and make up to 1L volume. The prepared phenol stock solution is stored in a cool place for later use. When needed, take a specific amount of the stock solution and dilute it to obtain the raw water with the required phenol concentration.

The RhB used in the experiment was prepared using pure water as a stock solution. The prepared Rhodamine B (RhB) stock solution had a mass concentration of 3000 mg/L. Precisely 3g of RhB was weighed on an analytical balance, dissolved, transferred to a volumetric flask, and diluted to a final volume of 1L. The prepared RhB stock solution was stored in a cool, dark place for later use. When needed, an appropriate aliquot of the stock solution was taken and diluted to obtain the required RhB concentration for the raw water.

The humic acid used in the experiment was prepared using pure water as a stock solution. The prepared humic acid stock solution had a mass concentration of 5000 mg/L. Accurately weigh 5g of dried humic acid powder, fully dissolve it in pure water under alkaline conditions with stirring, transfer the dissolved humic acid solution

to a volumetric flask, and make up to 1L volume. An appropriate aliquot of the stock solution was taken and diluted to prepare raw water with the desired humic acid concentration. The pH of the solution was then adjusted to neutral using dilute hydrochloric acid.

The ammonia nitrogen solution used in the experiment was prepared using ammonium chloride. The ammonium chloride used in the experiment was prepared using pure water as a stock solution. The prepared ammonium chloride stock solution had a mass concentration of 3000 mg/L. Accurately weigh 3g of ammonium chloride, transfer the dissolved ammonium chloride solution to a volumetric flask, and make up to 1L volume. The prepared ammonium chloride stock solution is stored in a cool place for later use. Each time, only a specific amount of the stock solution needs to be diluted to obtain the required ammonium chloride concentration raw water.

2.2 Experimental Setup

The experimental apparatus consisted of an ozone generator, flow meters, and four reaction columns. A schematic of the setup is presented in Figure 1. The reaction columns were constructed from polyvinyl chloride (PVC), each with a height of 80 cm and an inner diameter of 4.4 cm. The bottom of the carbon column was sequentially filled with support layers of 6 mm and 4 mm diameter glass beads to prevent loss of granular activated carbon due to inflow. The height of the glass bead layer was 5 cm, and the height of the activated carbon bed was 35 cm. The ozone reaction column was filled with 30 cm of glass beads to reduce ozone bubble size and ensure uniform gas distribution. Ozone was generated by the ozone generator and introduced from the bottom of the reaction column via flow meter control. Raw water was injected into the reaction column using a peristaltic pump, with an upflow mode of operation. The processes were divided based on the flow rate at the flow meter outlet into two processes: the traditional Ozone-Activated Carbon process (O_3-C process) and the integrated Ozone-Activated Carbon process (O_3/C process). The O_3-C process simulated the existing ozone-activated carbon process in water treatment plants, consisting of an ozone reaction column and an activated carbon reaction column. The O_3/C process is also an improved ozone-activated carbon process. O_3/C-1 and O_3/C-2 are both O_3/C processes with identical parameters, used for parallel experiment error analysis.

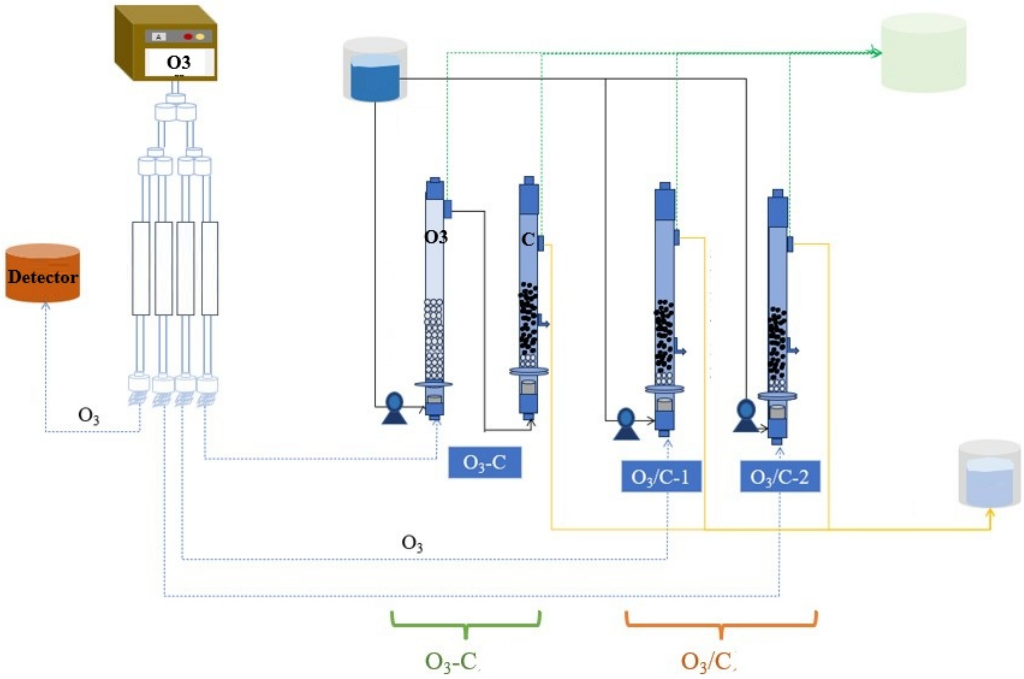

Figure 1 Schematic diagram of ozone activated carbon experimental device

Fresh activated carbon of equal mass was placed in both the O_3-C and O_3/C processes. The O_3-C process consisted of an ozone reaction column and an activated carbon column. Ozone and raw water entered from the bottom of the ozone reaction column. After ozone oxidation in the ozone reaction column, the water exited from the top outlet and entered from the bottom of the activated carbon column. After treatment by activated carbon adsorption in the activated carbon column, the water was discharged from the top outlet of the activated carbon column. The O_3/C process combined activated carbon and ozone in the same unit. Raw water and ozone entered through different inlets at the bottom of the ozone-activated carbon column. The raw water underwent simultaneous ozone oxidation and activated carbon adsorption inside the reaction column before exiting from the top outlet.

2.3 Analytical Methods

(1) Detection of Ozone Concentration in Water

The ozone concentration in water was determined by the iodometric method, according to the measurement of ozone concentration, yield, and power consumption of ozone generators (CJ/T3028.2-94). The method is based on the reaction of ozone with potassium iodide solution to generate free iodine. Place 20 mL of a 20% potassium iodide solution into a 250 mL ground glass conical flask and dilute to a specific volume. Next, bubble ozone gas through the solution for 60 seconds. Add 5 mL of dilute sulfuric acid solution, mix thoroughly, and allow the mixture to stand in the dark for 5 minutes. Titrate with a 0.01 mol/L sodium thiosulfate standard solution until the color turns pale yellow, then add 1 mL of starch indicator. Continue titrating until the blue color disappears and record the volume of sodium thiosulfate standard solution consumed.

(2) Phenol Concentration Detection Method

Phenol concentration was determined using a UV-Vis spectrophotometer. A phenol solution with a mass concentration of 20 mg/L was prepared by dissolving 0.2 g of phenol in a 1000 mL volumetric flask. Take an appropriate volume of the phenol solution and dilute it to 0, 5, 10, 15, 20 mg/L. Using ultrapure water as a blank control, scan in the wavelength range of 220~400 nm using the spectral scanning mode of the UV spectrophotometer. Based on the full wavelength scan results, the maximum absorption wavelength of phenol was determined to be 270 nm. Measure the phenol solutions at different gradient concentrations after dilution, and plot a standard curve using their absorbance.

(3) Rhodamine B Concentration Detection Method

Rhodamine B was measured using a UV-Vis spectrophotometer. Weigh 0.01g of Rhodamine B into a 1000 mL volumetric flask to prepare a Rhodamine B solution with a mass concentration of 10 mg/L. Take an appropriate volume of the Rhodamine B solution and dilute it to 1, 2, 3, 4, 5 mg/L. Using ultrapure water as a blank control, scan in the wavelength range of 220~660 nm using the spectral scanning mode of the UV spectrophotometer. Based on the full wavelength scan results, the maximum absorption wavelength of Rhodamine B was determined to be 554 nm. Measure the Rhodamine B solutions at different gradient concentrations after dilution, and plot a standard curve using their absorbance.

(4) Humic Acid Concentration Detection Method

Humic acid was measured using a UV-Vis spectrophotometer. Weigh 0.01g of humic acid into a 1000 mL volumetric flask to prepare a humic acid solution with a mass concentration of 10 mg/L. Take an appropriate volume of the humic acid solution and dilute it to 1, 2, 3, 4, 5 mg/L. Using ultrapure water as a blank control, UV254nmwas used indirectly to represent the humic acid absorption wavelength. Measure the humic acid solutions at different gradient concentrations after dilution, and plot a standard curve using their absorbance.

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3 Results and Discussion

3.1 Treatment Effect on Phenol-Containing Raw Water

The raw water was evenly distributed to the two parallel experimental processes, O_3-C and O_3/C, using a metering pump. The experiment was conducted in continuous operation mode, with regular monitoring of the residual concentration and related indicators at different sampling ports. The experimental results are presented in Figure 3.1. As shown in Figure 2a, when the influent phenol concentration varied between 2 mg/L and 5.5 mg/L, both the O_3/C and O_3-C processes demonstrated effective phenol removal over approximately 450 hours of operation. The O_3/C process achieved a phenol removal rate close to 100% in the effluent, while the O_3-C process also attained a removal efficiency of 99.69%. The figure shows that the phenol concentration in the ozone effluent (O_3 stage) of the O_3-C process fluctuated significantly, but the fluctuation trend did not completely correspond to the fluctuation of the influent concentration, indicating that for low concentrations of phenol in water, standalone ozone oxidation cannot effectively completely decompose phenol molecules, and will show different decomposition effects with changes in raw water quality. Therefore, O_3 must be combined with the activated carbon adsorption process for effective removal. Although the effluent phenol removal concentrations of the O_3/C and O_3-C processes appear almost identical from the figure, as mentioned above, in the traditional ozone-activated carbon process where ozone and activated carbon are separated, the activated carbon bears the entire burden of the intermediate products generated after ozone treatment and the trace organic matter in the raw water that ozone failed to remove effectively. Moreover, ozone and activated carbon cannot effectively synergize, and the utilization efficiency of the ozone oxidation stage is also low. In contrast, the O_3/C process integrates ozone oxidation and activated carbon adsorption synchronously, maximizing the synergistic effect of the two, resulting in more stable effluent quality. In the figure, the O_3-C process effluent showed short-term increases at 260-320 hours and 420 hours, indicating that the treatment effectiveness of the O_3-C process may be more affected by the ozone oxidation effect, and the activated carbon itself has poor removal effects on some O_3 oxidation products. In the O_3/C process, O_3, activated carbon, and trace phenol can undergo enrichment reactions on the activated carbon surface, which would increase the reaction speed and efficiency. Meanwhile, catalytic reactions of O_3 may also occur in the local environment, which can be verified by subsequent detection of other indicators [12].

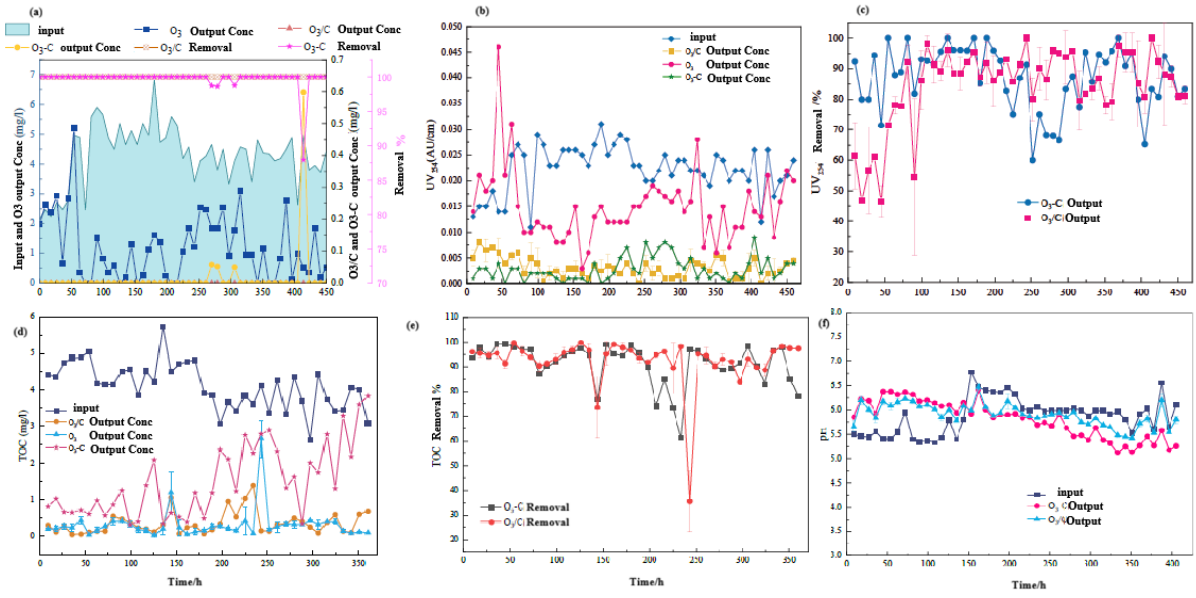

Figure 2 Removal efficiency of phenol by two processes; Comparison of UV254 removal effects between two processes (b); Comparison of UV254 removal rates between two processes (c); Changes in TOC concentration in inlet and outlet water of two processes （d; Changes in TOC removal rate of effluent from two processes (e); Changes in pH values of inlet and outlet water for two processes (f)

The UV254value is the absorbance of organic matter in water at a wavelength of 254 nm, reflecting the amount of naturally occurring humic-like macromolecular organic matter and aromatic compounds containing C=C double bonds and C=O double bonds in water. Phenol has a benzene ring structure and is therefore classified as an aromatic compound. After ozone oxidation breaks the unsaturated bonds of aromatic compounds, activated carbon adsorption plays an effective role. From Figure 2b, the UV254concentration of the raw water in the experiment was concentrated in the range of 0.01 mg/L to 0.0325 mg/L; after ozone oxidation and activated carbon adsorption, the UV254index in the effluent of both the O_3/C and O_3-C processes decreased significantly, reaching levels of 0 mg/L to 0.01 mg/L. Within 450 hours of operation, the effect of the standalone ozone (O_3 stage) effluent fluctuated greatly, with a removal rate of only about 60%. The average UV254removal rates of the combined O_3/C and O_3-C processes reached 84.6% and 87.1%, respectively, with roughly similar removal effects. However, from Figure 3.2, it can be seen that the effluent stability of the O_3/C process after a certain period of operation was better than that of the O_3-C combined process. The O_3-C integrated process exhibited high performance during the initial operational phase, likely attributable to the initially strong adsorption capacity of the activated carbon. As the activated carbon adsorbed the byproducts of ozone decomposition, its adsorption capacity within the O_3-C system gradually diminished, while its biodegradation capacity concurrently increased. The alternation of these two factors led to changes in effluent quality. Conversely, in the O_3/C process, due to the oxidation of substances on the surface and within the pores of the fresh activated carbon by ozone, the effluent quality fluctuated initially. However, as the reaction proceeded, a stable reaction balance was reached among ozone, activated carbon, and pollutants, at which point the effluent quality stabilized.

TOC (Total Organic Carbon) is employed to quantify the organic matter content in water, representing the total carbon mass derived from both dissolved and suspended organic compounds. This includes natural organic matter (NOM) as well as synthetic organic substances. From the changes in effluent phenol concentration mentioned above, it can be seen that after ozone oxidation and activated carbon adsorption, the effluent phenol concentration decreases significantly. This experiment further determined the reasons for the removal effect of influent phenol concentration by measuring the change in effluent TOC value. From Figure 2d, the TOC concentration of the raw water during the experimental phase was concentrated in the range of 2.5 mg/L to 5.5 mg/L. After ozone oxidation and activated carbon adsorption, TOC in the effluent of both O_3/C and O_3-C processes was effectively removed, with effluent concentrations ranging from 0 mg/L to 1 mg/L. From Figure 2e, the average TOC removal rates of the O_3/C and O_3-C process effluents were 92.5% and 91.2%, respectively, and the removal effect of the O_3/C process was more stable. Both processes can almost completely remove phenol, but some products of phenol removal still remain in the effluent. The lower residual content in the O_3/C process effluent indicates that the O_3/C process can more effectively remove trace phenol from water. In the O_3-C process, because the O_3 and activated carbon units are set separately, O_3 oxidation converts phenol into various intermediate products. Due to differences in the adsorption effectiveness of the subsequent activated carbon for different products, the overall removal efficiency of the O_3-C process is slightly lower.

From Figure 2f, it can be seen that the influent is weakly acidic. This is because phenol itself is weakly acidic, and the hydroxyl group (·OH) in the phenol molecule can release protons (H^+), resulting in an influent pH between 5 and 7. The effluent pH after treatment by the O_3/C and O_3-C processes remains weakly acidic. Under acidic conditions, phenol mainly exists in molecular form. After ozone oxidation and activated carbon adsorption, phenol molecules generate acidic substances such as CO_2 and haloacetic acids, making the effluent weakly acidic. It can be seen that the effluent pH of both O_3/C and O_3-C processes is relatively stable and not significantly different from the influent. However, the effluent pH of the O_3/C process is closer to the raw water pH compared to the O_3-C process, while the effluent pH of the O_3-C process tends to decrease gradually over time.

3.2 Removal Effect on RhB-Containing Raw Water

The RhB raw water was prepared daily and simultaneously distributed to the two parallel experimental columns (O_3-C and O_3/C) using a metering pump. The experiment was conducted in continuous operation mode to compare the removal effects of the two technologies on RhB. The experimental results are shown in Figure 3.

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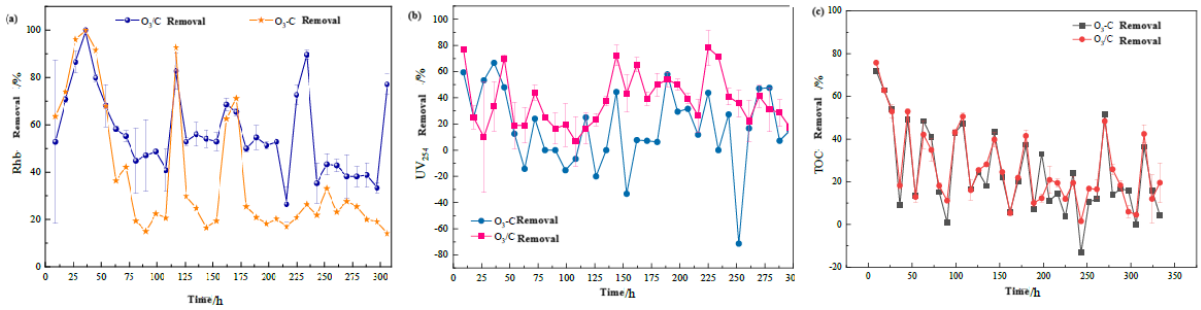

Figure 3 Removal rates of RhB by two processes in RhB experiment (a); Changes in UV254 removal rate of effluent from two processes in RhB experiment (b); Removal rates of TOC by two processes in RhB removal experiment(c)

From Figure 3a, when the RhB concentration of the raw water fluctuated in the range of 0.2 mg/L to 1.7 mg/L; after nearly 60 hours of operation, the removal rates of RhB by both the O_3/C and O_3-C processes could reach 90% initially. As the influent concentration decreased, the removal efficiency observed in the effluent also declined. The O_3/C process achieved an average RhB removal rate of approximately 57% in the effluent, while the O_3-C process showed an average removal rate of about 41%. Moreover, the RhB concentration in the ozone effluent (O_3 stage) of the O_3-C process fluctuated significantly, with a low removal rate, indicating that for trace RhB in water, standalone ozone oxidation cannot effectively completely decompose RhB molecules. This results in the O_3 and activated carbon in the O_3-C process separately bearing the burden of RhB removal, leading to poor removal efficiency. In contrast, the O_3/C process, due to the synchronous contact between O_3 and activated carbon, creates mutual synergistic catalytic effects among O_3, activated carbon, and pollutants, thus significantly improving the treatment effect, with a removal rate nearly 1.5 times that of the O_3-C process. RhB is a refractory substance, and standalone activated carbon adsorption is also relatively ineffective. Usually, processes that generate highly oxidizing •OH radicals are needed to promote improved removal efficiency. When O_3 transitions from the gas phase to the liquid phase, it generates •OH active free radicals. During the oxidation reaction of RhB by •OH active free radicals, the conjugated structure of the RhB molecule disintegrates, the nitrogen ethyl group detaches, and the benzene ring undergoes ring opening [13]. The poor direct removal effect of ozone on RhB may be because the influent pH, simulating real source water conditions, is neutral to weakly acidic. Research [14] has shown that compared to acidic conditions (pH=2~3), under neutral and alkaline conditions, the oxidation of organic matter produces •OH scavengers (such as CO_3^{2-}, HCO_3^-, etc.), thereby reducing the number of •OH active free radicals and their oxidation capacity. Meanwhile, the low concentration of Cl^- produced from ammonium chloride in the raw water inhibits the decomposition of ozone, hindering the chain reaction of •OH generation, and also reacts with some •OH to form less oxidizing •Cl, reducing the oxidation capacity of •OH [15], thus leading to a decrease in RhB degradation rate, as shown in Equation 1. In the O_3/C process, the active sites on the GAC surface can initiate O_3 to generate •OH active free radicals, and they can concentrate the reactants around them, thereby accelerating the degradation process of RhB molecules. This may be the reason for the better removal efficiency of the O_3/C process.

$$\cdot OH + Cl^- + H^+ \rightarrow \cdot Cl + H_2O \qquad (1)$$

Since RhB has an aromatic structure and has an absorption peak at 254 nm, UV254was used as one of the detection indicators for the degradation of RhB by the ozone-activated carbon process. From Figure 3b, the UV254concentration of the prepared RhB raw water was concentrated in the range of 0.009 mg/L to 0.11 mg/L; however, after ozone oxidation, the UV254concentration increased significantly. This is related to the characteristics of the UV254indicator. Since substances containing benzene rings have significant absorption peaks at 254 nm, the increase in UV254concentration indicates that after O_3 oxidation, RhB decomposes into a large amount of intermediate products containing benzene rings. In the O_3-C process, the intermediate products from the ozone effluent need to be effectively removed by the activated carbon unit. In practice, the adsorption effect of activated carbon usually depends on the molecular structure of the adsorbate. These intermediates containing benzene rings often have poor adsorption effects, resulting in an average UV254removal rate of only 23.64% for the O_3-C process effluent, as shown in Figure 3b. In contrast, the O_3/C process, for the reasons

mentioned earlier, has certain catalytic reactions and better treatment efficiency, with an average UV254removal rate of 40.94% for the effluent. This result also indicates that the O_3/C process has superior removal effects on complex trace organic matter in water compared to the O_3-C process.

The TOC removal effects of the O_3-C and O_3/C process effluents are shown in Figure 3c. From Figure 3c, the TOC removal rates of both the O_3/C and O_3-C process effluents are relatively low and similar. When the influent TOC concentration ranged from 2 to 11 mg/L, the effluent TOC typically remained between 2 and 3 mg/L. In contrast, the TOC concentration in the ozone oxidation effluent of the O_3-C process fluctuated between approximately 2 and 5 mg/L. From Figure 3.12, the average TOC removal rate of the O_3-C effluent was 22.17%, and that of the O_3/C effluent was 24.67%. The overall average removal rate of O_3/C was better than O_3-C. Based on the TOC removal effect combined with the RhB and UV254removal effects, it can be concluded that there are differences in the RhB removal processes between the O_3-C and O_3/C processes. The O_3-C process has lower removal effects on both RhB and UV254compared to the O_3/C process, but the effluent TOC concentrations are similar. This indicates that although the O_3/C process can effectively oxidize and decompose RhB, due to the significantly higher oxidation capacity of O_3/C compared to the O_3 oxidation capacity in the O_3-C process, it may produce more oxidation intermediate products. The amount of these intermediate products that can be adsorbed by activated carbon may be low, leading to their appearance as TOC in the effluent.

3.3 Treatment Effect on Humic Acid-Containing Raw Water

The humic acid raw water was prepared daily and distributed to the two parallel experimental columns (O_3-C and O_3/C) using a metering pump. The experiment was conducted in continuous operation mode to compare the removal effects of the two processes on the humic acid concentration in water. The experimental results are shown in Figure 4.

From Figure 4a, when the humic acid concentration of the raw water fluctuated in the range of 3~4 mg/L; after nearly 80 hours of operation, the removal efficiencies of humic acid concentration by both the O_3/C and O_3-C processes were relatively low. From Figure 4a, the average humic acid removal rate of the O_3/C process effluent was about 10.56%, and that of the O_3-C process effluent was about 12.82%. The experimental results show that the overall humic acid removal rate of the O_3-C process is higher than that of the O_3/C process. This phenomenon may be caused by the different operation modes of the two processes. The O_3/C process adopts an upflow integrated operation mode. Ozone and influent enter from the bottom of the reaction column and flow upward in a multiphase flow manner. The activated carbon filter material in the column is in a certain fluidized state, resulting in a low removal rate of insoluble substances in water. In contrast, the O_3-C carbon process adopts a downflow operation mode, which has high filtration and interception functions, resulting in good removal effects on insoluble suspended substances in water. The humic acid used in the experiment is poorly soluble in water, so it exists in a certain non-dissolved state in water. The humic acid concentration can be effectively removed by the adsorption and filtration effects of the activated carbon filter column in the O_3-C process, but the removal effect is poor under the operating conditions of the O_3/C process, resulting in a higher removal rate for the O_3-C process than for the O_3/C process.

Additionally, the figure shows that the humic acid concentration in the ozone effluent (O_3 stage) of the O_3-C process is mostly higher than the influent concentration. Considering the time difference between the reactor inlet and outlet, it can be concluded that standalone ozone oxidation cannot effectively decompose humic acid molecules. If such slightly soluble, high molecular weight complex organic matter in water is to be removed, it must rely on the adsorption or biodegradation of activated carbon [16]. Standalone O_3 may not effectively remove the humic acid concentration in water, possibly also because the humic acid raw water pH is neutral to weakly acidic. Under neutral and weakly acidic conditions, O_3 exists in molecular form in water, the generation of •OH is inhibited, the yield is reduced, and the oxidation of organic matter can only proceed via direct oxidation, which is slow and selective for the oxidized organic matter, leading to reduced •OH oxidation performance [17]. Therefore, the humic acid removal rates of both the O_3-C and O_3/C processes are low.

Research has shown [18] that the absorbance of humic acid at 254nm has a good linear relationship with its mass concentration, so UV254can be used to characterize the mass concentration of humic acid. At the same time, UV254can also reflect the number of unsaturated bonds in the humic acid structure; the more unsaturated

bonds, the higher the UV254value. From Figure 4b, it can be seen that both the O_3/C and O_3-C processes have good removal effects on UV254in the effluent. The UV254removal rate of the O_3/C process effluent ranged from 32.76% to 63.63%, with a maximum of 92.10%. The UV254removal rate of the O_3-C process effluent ranged from 37.93% to 68.42%, with a maximum of 100%. The humic acid concentration in the ozone effluent (O_3 stage) of the O_3-C process sometimes exceeded the influent humic acid concentration, indicating that standalone O_3 cannot effectively oxidize humic acid in water. This is because ozone can oxidize the unsaturated structure in humic acid molecules, reducing the number of unsaturated bonds, thereby reducing UV254[19]. The effluent after the O_3 stage, treated by activated carbon adsorption, can effectively remove organic matter containing unsaturated bonds, thus significantly reducing UV254.

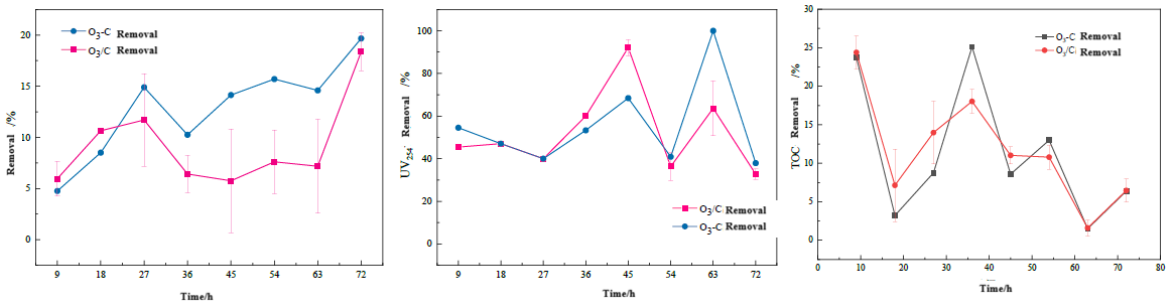

Figure 4 Removal rates of humic acid by two processes in the humic acid experiment (a);Removal rate of UV254 in humic acid experiment (b); Removal rate of TOC in humic acid experiment (c)

Studies have shown [20] that ozone oxidation is difficult to completely decompose humic acid; it usually only decomposes humic acid into various intermediate products. This experiment used TOC as an indicator to evaluate the amount of humic acid converted into intermediate products during the oxidation decomposition process. The experimental results are shown in Figure 4c. From Figure 4c, the TOC removal rates of the effluents from both the O_3/C and O_3-C processes are relatively low. The average TOC removal rate of the O_3/C process effluent is only 19.12%, while that of the O_3-C process effluent is only 25.12%. The low TOC removal rate indicates the following two points: First, the oxidation effect of ozone on humic acid is poor, as can also be seen from the experimental results. The low TOC removal rate of the standalone O_3 effluent reflects the difficulty of O_3 to completely decompose it. Second, the adsorption and biodegradation effects of activated carbon on humic acid are poor. The small difference between the TOC concentration of the activated carbon effluent and the O_3 effluent TOC concentration in the figure indicates that most of the products after ozone oxidation are difficult to be effectively removed by activated carbon.

By comparing the removal rates of humic acid concentration, UV254, and TOC between the two processes, it is found that both processes have low removal effects on humic acid concentration, relatively high removal rates for UV254in the effluent, and similar TOC removal effects. This is because the UV254and TOC indicators can indirectly reflect the decomposition process. Therefore, it can be concluded that ozone oxidation can partially decompose humic acid macromolecules, forming intermediate small molecule organic compounds such as oxalic acid, acetic acid, and pyruvic acid [20]. These organic compounds no longer have unsaturated structures like benzene rings, so UV254shows a high removal effect, but the substances still exist in the water in organic form, hence the low removal effect of effluent TOC concentration.

From the experimental results, it can be seen that the humic acid and TOC removal rates of the O_3/C process are lower than those of the O_3-C process, but the UV254removal rate is relatively higher. The reason may be that when O_3 does not contact activated carbon, its oxidation process is mostly direct oxidation, producing fewer •OH free radicals and having a weaker oxidation decomposition capacity for humic acid. In the O_3/C process, the direct contact between O_3 and activated carbon catalyzes the ozone, stimulating O_3 molecules to produce more •OH [21], therefore the UV254removal effect of the O_3/C process is higher than that of the O_3-C process.

4 Conclusion

This paper primarily compared the removal effects of the O_3/C and O_3-C processes on pollutants of different properties. The effluent from the O_3/C and O_3-C processes was measured for organic matter concentration, UV254, TOC, pH, CODMn, ammonia nitrogen, and turbidity. The experimental ozone dosage was determined through ozone dosage experiments. The main conclusions are as follows: (1) When phenol was the pollutant, the phenol removal rates of the O_3/C and O_3-C process effluents were nearly 100% and 99.69%, respectively. The average UV_{254} removal rates were 84.6% and 87.1%, respectively, while the average TOC removal rates reached 92.5% and 91.2%, respectively. The effluent pH of the O_3/C process remained closer to the influent pH compared to that of the O_3‑C process. The removal effect of the O_3/C process was superior to that of the O_3-C process. (2) When RhB was the pollutant, the average RhB removal rates of the O_3/C and O_3-C process effluents were 57% and 41%, respectively. The average UV254removal rates reached 40.94% and 23.64%, respectively, and the average TOC removal rates were 24.67% and 22.17%, respectively. The effluent pH of both the O_3/C and O_3-C processes was not significantly different from the influent and showed a similar trend of change as the raw water. The removal effect of the O_3/C process was superior to that of the O_3-C process. (3) When humic acid was the pollutant, the average humic acid removal rates of the O_3/C and O_3-C process effluents were 10.56% and 12.82%, respectively. The average UV254removal rates reached 52.17% and 55.28%, respectively, and the average TOC removal rates were 19.12% and 25.12%, respectively. The effluent pH of the O_3/C process was higher than the influent, while the effluent pH of the O_3-C process was lower than the influent. The removal effects of humic acid by the O_3/C and O_3-C combined processes were roughly the same. The removal effects of phenol, RhB, humic acid, UV254, and TOC in the ozone effluent (O_3 stage) of the O_3-C process were all poor. Combined with the analysis that the O_3-C process effluent showed short-term increases multiple times, this indicates that the treatment effect of the O_3-C process may be significantly affected by the ozone oxidation effect.

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