

Article

Catalytic Ozonation of Reactive Red 195 in Aqueous Solution over a Cobalt/Aluminum Oxide-Ceria Catalyst

Bi-Hong Lv *, Xiao-Yu Liu, Zhuo-Ming Zhou and Guo-Hua Jing

Department of Environmental Engineering, Huaqiao University, Xiamen 361021, China; liuxy19871030@126.com (X.-Y.L.); zzm1975@126.com (Z.-M.Z.); zhoujing@hqu.edu.cn (G.-H.J.)
* Correspondence: lbh1225@hqu.edu.cn

Abstract: The textile industry has become one of the largest producers of water pollution. The azo dyes used in the textile industry may present a serious environmental problem because of their high toxicity and chemical stability. In the present work, the cobalt/aluminum oxide-ceria (Co/Al₂O₃-CeO₂) catalyst was synthesized, and the degradation of Reactive Red 195 (RR195) by catalytic ozonation was studied. The Co/Al₂O₃-CeO₂ catalyst was synthesized via the incipient wetness method with the assistance of ultrasound. The presence of Co/Al₂O₃-CeO₂ did not notably improve the degradation of RR195 compared to ozonation alone, but it was advantageous for RR195 mineralization. The effects of initial dye concentration (200–800 mg/L), catalyst dosage (1–4 g/L), and solution pH (4–10) on color, and COD removal were evaluated. The results indicate that the dye's concentration significantly affects COD removal efficiency. The optimum catalyst dosage and pH values were determined to be 3 g/L and 8, respectively. Co/Al₂O₃-CeO₂ catalyst shows good catalytic activity and stability based on four repeated tests during RR195 ozonation. Finally, a possible mechanism and a kinetic scheme of the catalytic ozonation of RR195 were proposed.

Keywords: dye removal; catalytic ozonation; Co/Al₂O₃-CeO₂; Reactive Red 195



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1. Introduction

The textile industry has become one of the largest producers of industrial wastewater, and dyes are major pollutants that come from these textile wastewaters [1]. The majority of dyes used in the textile industry are azo dyes, which are toxic, recalcitrant, chemically stable, and carcinogenic. Their release into the environment may pose many serious aesthetic, ecological, environmental, and health hazards [2]. Therefore, the discarding of these dyes must be controlled, and the effluents must be treated [3]. Different physical and biological methods, or combinations of them, have been investigated for color removal from dye-laden wastewater. However, they all suffer from specific disadvantages [2].

In recent years, chemical treatment processes, especially chemical oxidation, have become the method of choice due to their high efficiency and easy operation [4,5]. Ozone is one of the most effective oxidant agents used for decolorization of dyes owing to its extremely high redox potential ($E_0 = 2.07$ V). During ozonation, conjugated double bonds, which are often associated with color, can be broken down by ozone either directly or indirectly [3,5,6]. Although single ozonation has been shown to be effective for color removal, the formed intermediates are frequently resistant to ozone attack and the mineralization extent is usually insufficient [5]. In order to improve efficiency, various advanced oxidation processes (AOPs, e.g., O₃/H₂O₂, UV/O₃, catalytic ozonation, etc.) have been investigated. Especially heterogeneous catalytic ozonation has received increasing attention in recent years due to its potentially high effectiveness in the degradation of harmful organic pollutants with low negative effects on the environment [7].

Different metals or their oxides (such as Co, Fe, Ni, and manganese oxides) deposited on porous materials (such as alumina, activated carbon, and MCM-41) were investigated

as the catalysts for catalytic ozonation [8–10]. Ceria (CeO_2), which can act as a reducible support or catalyst itself, has been extensively applied in heterogeneous catalysis due to its unique property of storing and releasing oxygen (redox property) and its excellent thermal and mechanical resistance [11–13]. Several works found that palladium oxide (PdO) loaded CeO_2 catalyst could promote the degradation of pyruvic acid and oxalate in water by catalytic ozonation better than ozonation alone [11,14,15]. However, the CeO_2 carrier suffers from the disadvantages of high cost and relatively low surface areas [13]. Therefore, deposition of ceria on a high surface area support, like alumina, was achieved. Adding cerium to alumina produces structural changes, improves the dispersion of the metal, and stabilizes the alumina to avoid thermal sinterization [16]. Due to the advantageous properties mentioned above, CeO_2 - Al_2O_3 has been used extensively as a potential support, such as in the generation of hydrogen by methane reforming and in the elimination of pollutants (such as NO_x , CO, and hydrocarbons) in automobile exhausts [17]. Chen et al. [18] found that the Al_2O_3 - CeO_2 catalysts were active for CH_2Cl_2 catalytic combustion, and that the activity could be further promoted by the addition of Pt. Li et al. [19] found that the introduction of CeO_2 into the $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst improved the dispersion of CuO on the catalyst surface. In addition, the specific surface area and pore volume of the samples gradually decreased with the increase in CeO_2 content. The synergistic effect ($\text{Ce}^{3+} + \text{Cu}^{2+} \leftrightarrow \text{Ce}^{4+} + \text{Cu}^+$) favors the generation of oxygen vacancies and increases the activity of the catalyst. Zhou et al. [20] modified the conventional $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst with CeO_2 and increased the proportion of Pt^0 from 74.5% to 82.1%. When the metal state Pt^0 content is increased, the redox activity of the catalyst increases accordingly. Li et al. [17] systematically investigated the synergistic effect of Al_2O_3 and CeO_2 on MIAA (monoiodoacetic acid)-catalyzed hydrodeiodination (HDI). Experimental characterization shows that the introduced CeO_2 can improve the dispersion of Pt by forming a Ce-O-Pt bond and that the high zeta potential of the Al_2O_3 component can facilitate the adsorption of MIAA. Through kinetic experiments and characterization, the abundance of Pt sites and the synergistic interaction between CeO_2 and Al_2O_3 allow Pt/CeO_2 - Al_2O_3 to exhibit excellent catalytic performance. In other studies, a $\text{Pt}/\text{Al}_2\text{O}_3$ - CeO_2 nanocatalyst was used to oxidize volatile organic compounds (VOCs) and toluene, it also showed good catalytic performance [12,13].

As above-mentioned, several catalysts based on Al_2O_3 - CeO_2 have been reported to be able to catalytic oxidation of organic compounds but seldom have been used in the catalytic ozonation of azo dyes. To better understand the potential use of this carrier, in this work, the $\text{Co}/\text{Al}_2\text{O}_3$ - CeO_2 catalyst was synthesized, and the degradation of Reactive Red 195 (RR195) by catalytic ozonation was studied. The influence of solution pH, initial dye concentration, ozone dosage, and catalyst dosage were assessed in catalytic ozonation of RR195. Finally, the mechanism and kinetics model of RR 195 degradation was established.

2. Materials and Methods

2.1. Materials

RR 195 was obtained from Quanzhou Anze Dyestuff Chemical Factory (Quanzhou, China). Cerium nitrate (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Cobalt acetate (AR) was purchased from Shanghai Reagent Factory (Shanghai, China). γ - Al_2O_3 was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Other chemicals and reagents were purchased from Shantou Xilong Chemical Works (Shantou, China). Distilled water was used in preparing the solution for all the experiments.

2.2. Catalysts Preparation

The Al_2O_3 - CeO_2 support was prepared by impregnating γ - Al_2O_3 with cerium nitrate aqueous solutions following the incipient wetness method [21]. The γ - Al_2O_3 was doped with 20 wt% cerium nitrate. The samples were sonicated in ambient air for 3 h and then impregnated for 12 h. The impregnated samples were dried at 105 °C for 2 h and finally calcined in air at 450 °C for 2 h.

The Co/Al₂O₃-CeO₂ catalyst was prepared by impregnating Al₂O₃-CeO₂ with a cobalt acetate aqueous solution according to the incipient wetness method with the assistance of ultrasound [22]. The calculated Co content (wt.%) loaded on the catalyst was 4%. The samples were sonicated in ambient air for 3 h and impregnated for 12 h. After impregnation, the sample was dried at 105 °C for 2 h. Then the Co/Al₂O₃-CeO₂ catalysts were formed by calcination at 450 °C for 2 h.

2.3. Experimental Setup

Ozonation and catalytic ozonation of RR195 were carried out in a semi-batch mode apparatus, which consisted of an oxygen cylinder, an ozone generator (CF-G-3-10g), a flow meter, an ozone reactor (8 cm internal diameter × 40 cm height) and an ozone off-gas destruction system, and the detailed description is shown in our previous report [23]. Before the start of the experiment, the reactor was filled with 500 mL RR195 solution, and the catalyst was introduced into the reactor. The mixtures were stirred for 10 min by a magnetic stirrer. After that, the ozonized oxygen, produced from the ozone generator, flowed into the reactor through a gas flow meter for 20 more minutes. Water samples were collected from the reactor at specific predetermined times to analyze RR195 and COD concentrations. A gas absorption bottle containing 10% Na₂S₂O₃ solution was used to destroy the remaining ozone before leaving the reactor.

2.4. Analytical Methods

The crystal structure of the catalysts was emphasized by X-ray diffraction (XRD) with a BRUKER D8 Advanced analyzer (Bruker, Germany). The particle size distribution of Co/Al₂O₃-CeO₂ was performed using a Mastersizer 2000 laser particle size analyzer (Malvern, USA). The concentrations of ozone in the gas phase were measured by iodometric titration [24]. The concentrations of ARB solution were determined by measuring the absorbance of the solution at 514 nm with a UNICO UV-4802H spectrophotometer (Unico, America).

COD_{Cr} was determined by a rapid microwave-sealed digestion method by K₂Cr₂O₇. Using a pipette to draw 10 mL of water sample into the digestion tank, and 5 mL of K₂Cr₂O₇ digestion solution and 10 mL of HNO₃-AgNO₃ were added. After shaking and sealing tightly, the tank was put into the digestive chamber for 15 min. After the digestion, the reaction solution was transferred to a 150 mL conical flask, and the indicator test ferroin and ferrous ammonium sulfate hexahydrate standard solution were added. When the color of the solution changed from yellow through blue-green to red-brown, that is the end of the titration.

3. Results and Discussion

3.1. Catalyst Characterization

The particle size distribution of Co/Al₂O₃-CeO₂ is given in Figure S1. The median particle diameter of Co/Al₂O₃-CeO₂ was 22.472 μm, and the volume mean diameter of Co/Al₂O₃-CeO₂ was 36.153 μm. The XRD patterns of γ-Al₂O₃ support, Co/Al₂O₃, and Co/Al₂O₃-CeO₂ are shown in Figure 1. Three well-resolved reflections (at 2θ = 37.77°, 45.79° and 66.76°) were seen for γ-Al₂O₃. The diffraction peaks of cobalt species were observed at 2θ = 37.1° both in Co/Al₂O₃ and Co/Al₂O₃-CeO₂ samples, indicating that cobalt species are dispersed across the supports. Moreover, the formation of CeO₂, as indicated by the diffraction peak at 2θ = 28.7°, 33.2°, 47.7° and 56.6°, corresponds to CeO₂ in the Co/Al₂O₃-CeO₂ sample.

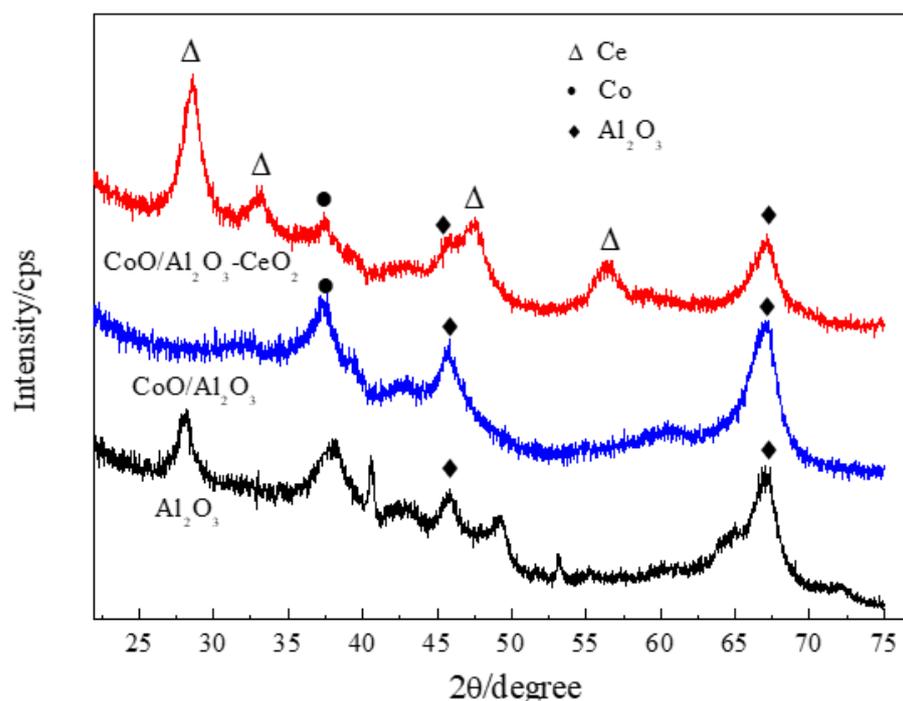


Figure 1. The XRD pattern of Al_2O_3 , $\text{Co}/\text{Al}_2\text{O}_3$, and $\text{Co}/\text{Al}_2\text{O}_3\text{-CeO}_2$.

3.2. Catalytic Ozonation of RR 195

Figure 2 compares the color and COD degradation of RR195 for O_3 alone, $\text{Co}/\text{Al}_2\text{O}_3/\text{O}_3$, and $\text{Co}/\text{Al}_2\text{O}_3\text{-CeO}_2/\text{O}_3$ processes. As can be observed in Figure 2, the RR 195 removal efficiency of single ozonation was lower than that of catalytic ozonation at the first 15 min. However, the efficiencies all increased to almost 100% when the reaction time was extended to 20 min. This means that ozone is very efficient in RR195 removal. In addition, compared with single ozonation, it was found that both the $\text{Co}/\text{Al}_2\text{O}_3\text{-CeO}_2$ catalyst and the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst can improve COD removal efficiencies of RR195. However, the $\text{Co}/\text{Al}_2\text{O}_3\text{-CeO}_2/\text{O}_3$ process is the most efficient one. During the ozonation (200 mL/min ozone flow rate) of 400 mg/L of RR195 (pH 8.0), after 10 min, COD removal efficiency was only 20%, whereas the values reached 53% and 43%, respectively, after adding $\text{Co}/\text{Al}_2\text{O}_3\text{-CeO}_2$ and $\text{Co}/\text{Al}_2\text{O}_3$ as a catalyst. After 30 min, the COD removal efficiencies achieved 87% and 72% by using $\text{Co}/\text{Al}_2\text{O}_3\text{-CeO}_2$ and $\text{Co}/\text{Al}_2\text{O}_3$ catalysts, respectively, which were higher than that of the ozonation alone (62%).

From the above results, it can be seen that in a single ozonation process, RR 195 suffered a quick degradation achieving up to nearly 100%, but only a low mineralization degree was achieved with about 62% of final COD removal after 30 min. This may be due to the strong electrophilic nature of ozone molecule that reacts directly with nucleophilic positions of aromatic rings. Nevertheless, the accumulation of different refractory intermediates during the ozonation process leads to a low level of mineralization [25]. It was also found that $\text{Co}/\text{Al}_2\text{O}_3\text{-CeO}_2$ shows higher catalytic activity for efficient mineralization of RR 195 than that of $\text{Co}/\text{Al}_2\text{O}_3$. As previously reported [26,27], cerium oxide prepared from Ce(III) salt aqueous solutions can result in CeO_2 containing traces of Ce(III), which are thought to be necessary for promoting the decomposition of ozone into hydroxyl radicals by redox reactions on the catalyst surface. Another role that CeO_2 played is to improve metal dispersion, which is believed to increase the active sites of the catalyst [16,26]. Due to these two reasons, in this case, the catalytic activity of the $\text{Co}/\text{Al}_2\text{O}_3\text{-CeO}_2$ catalyst is higher than that of the $\text{Co}/\text{Al}_2\text{O}_3$, thus leading to a higher mineralization of RR 195.

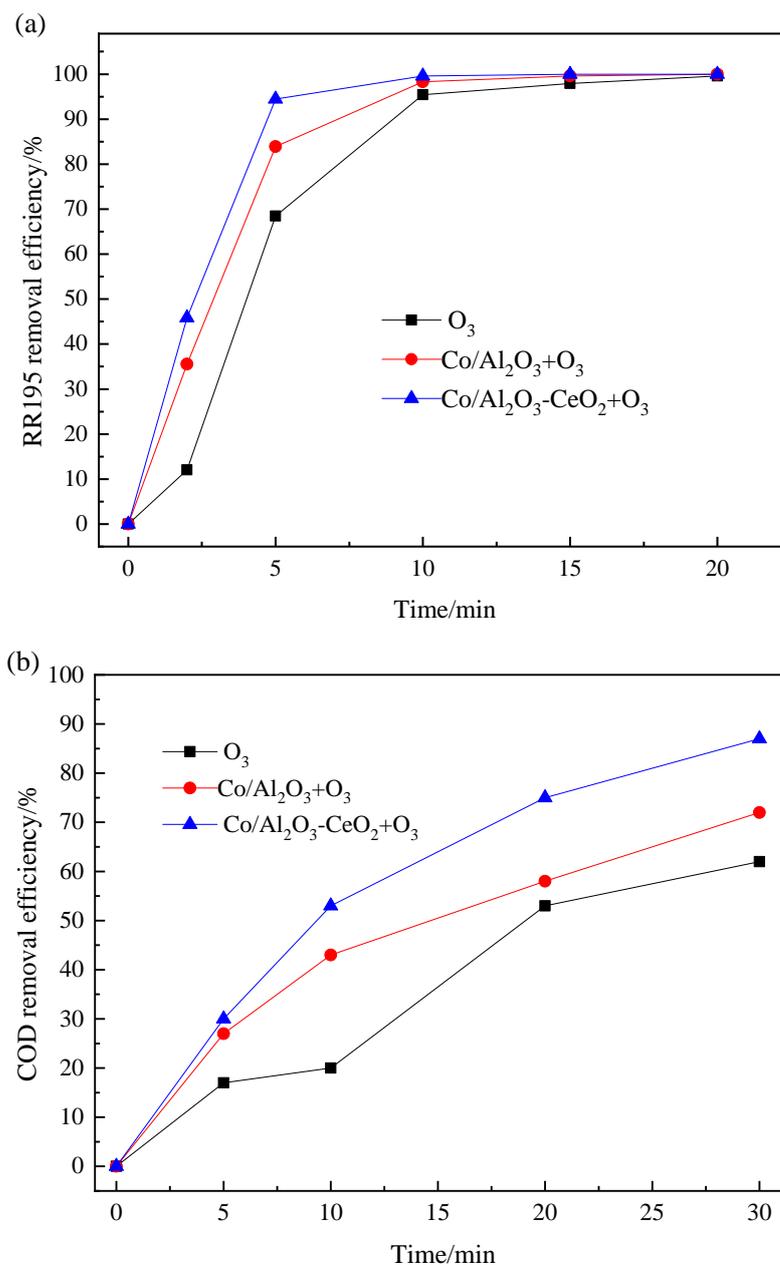


Figure 2. Comparison of the RR195 removal with and without catalytic ozonation: (a) RR195 removal efficiency; (b) COD removal efficiency. (RR195 concentration 400 mg/L, pH 8, gas flow 200 mL/min, ozone flow 6 mg/min, catalyst dosage 3 g/L, magnetic stirring speed 1400 rpm).

3.3. Effect of Initial RR 195 Concentrations

Figure 3 depicts the effect of initial RR195 concentrations on RR195 and COD removal by the $Co/Al_2O_3-CeO_2$ catalytic ozonation process. It was observed that, after 5 min, RR195 removal efficiencies were 93%, 84.3%, 78%, and 75% when initial RR195 concentrations were 200, 400, 600 and 800 mg/L, respectively, indicating that the removal efficiencies decreased with increasing RR195 initial concentrations. However, after 20 min, the RR195 removal efficiencies were all close to 100%. In the case of COD removal efficiencies, the values were 89%, 78.5%, 65.4%, and 60.6% after 20 min with initial RR195 concentrations of 200, 400, 600, and 800 mg/L, respectively. With increasing RR195 concentrations, COD removal efficiency decreased more significantly than that of RR195 removal efficiency. These findings show that the dye's concentration has no significant influence on RR195 removal within the tested range. However, it significantly affects COD removal efficiency.

This may be because of a greater affinity of ozone with dye compounds than with their by-products, and thus, more organic intermediates may generate and accumulate in the reactor with increasing initial dye concentrations, which contributes to COD measurement other than RR195 measurement [28].

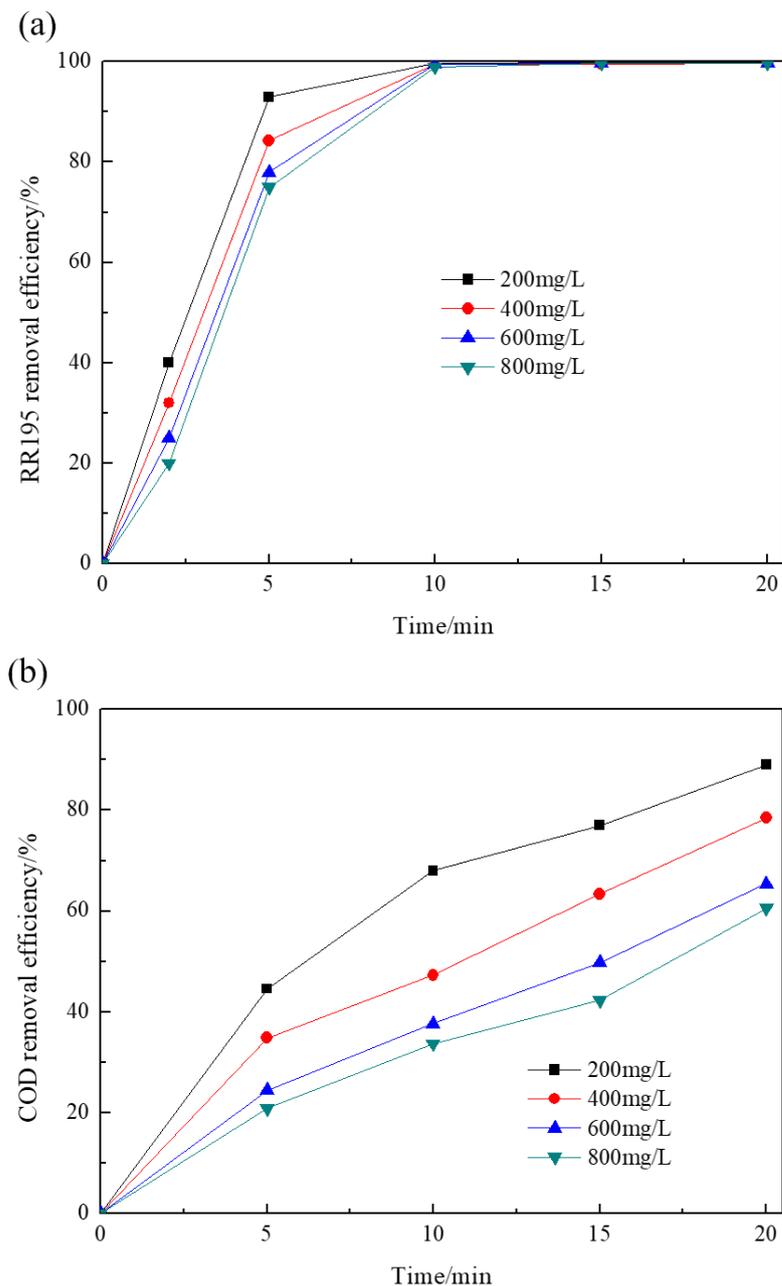


Figure 3. Effect of initial RR195 concentrations on RR195 removal in the catalytic ozonation: (a) RR195 removal efficiency; (b) COD removal efficiency. (pH 7, gas flow 200 mL/min, ozone flow 6 mg/min, catalyst dosage 3 g/L, magnetic stirring speed 1400 rpm).

3.4. Effect of Catalyst Dosage

The catalytic ozonation of RR195 in the presence of various dosages of the Co/Al₂O₃-CeO₂ catalysts (ranging between 1 g/L and 4 g/L) was evaluated. As shown in Figure 4, within 20 min of the reaction, COD removal efficiency of RR195 increased gradually, from 68.4% to 75.2%, 78.9%, and 79.2%, with increasing catalyst edge from 1 to 2, 3, and 4 g/L, respectively. These results further illustrate the effectiveness of Co/Al₂O₃-CeO₂ as a catalyst in catalyzed ozonation. Moreover, as previously reported [29], increasing

the catalyst loading could improve the organic compound removal efficiency. The results indicate that some other more effective oxidant (such as hydroxyl radical) may be generated when catalysts are used in the ozonation process. In addition, it was found that the removal efficiency increased faster at lower dosages (from 1 to 3 g/L) than at higher dosages (from 3 to 4 g/L). This phenomenon is possibly because, at higher catalyst concentrations, more hydroxyl radicals are produced, and more hydroxyl radicals will combine with each other [29]. Therefore, 3 g/L Co/Al₂O₃-CeO₂ was determined as the optimum dosage for RR195 ozonation in the present work and was used in all remaining experiments.

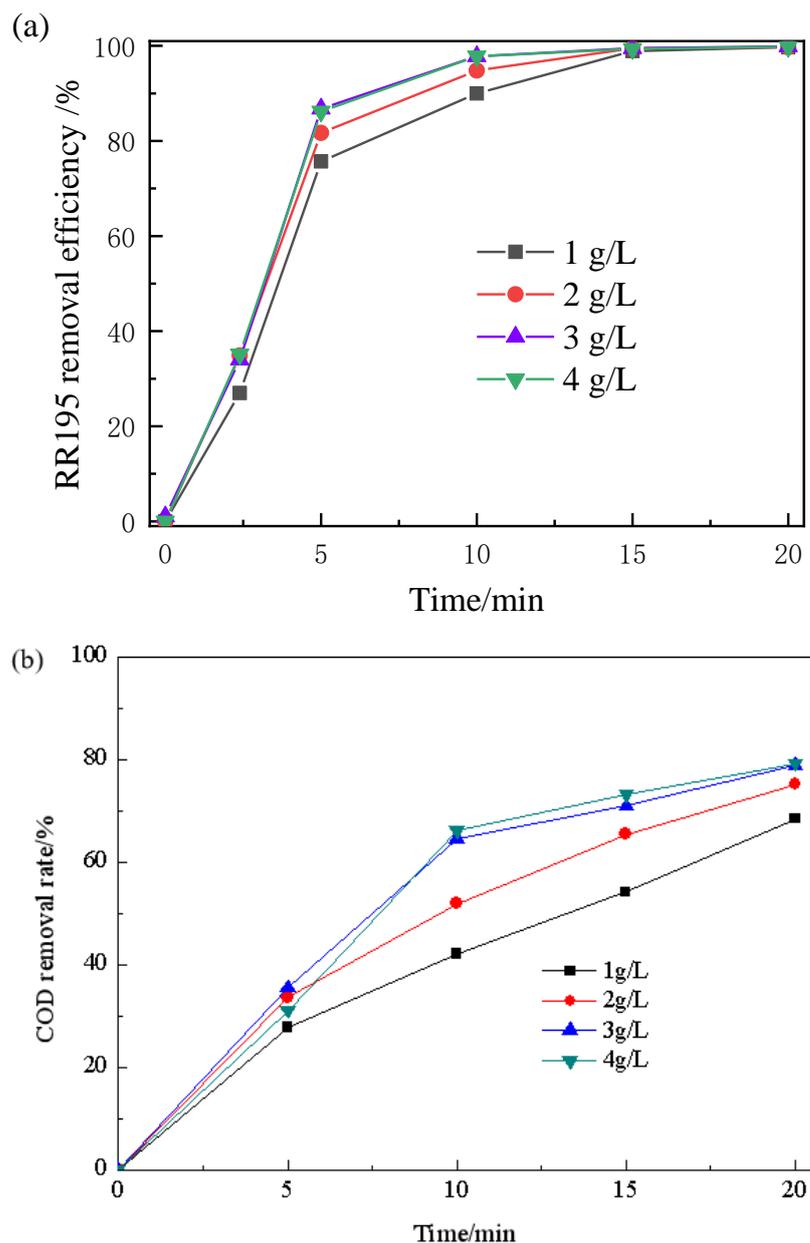


Figure 4. Effect of Co/Al₂O₃-CeO₂ dosage on RR195 removal in the catalytic ozonation: (a) RR195 removal efficiency; (b) COD removal rate. (pH 7, gas flow 200 mL/min, ozone flow 6 mg/min, RR195 concentration 400 mg/L, magnetic stirring speed 1400 rpm).

3.5. Effect of pH

The effect of solution pH on COD removal of RR195 was studied with pH ranging from 4 to 10. In a single ozonation process, it can be seen from Figure 5 that increasing

the initial pH from acidity to basicity led to an enhancement in RR195 and COD removal. After 20 min, the RR195 removal efficiencies were nearly 100% for all pH. However, COD removal efficiencies were 53%, 55%, 60%, and 63% at pH 4, 6, 8, and 10, respectively. COD removal efficiency increases as pH increases from 4 to 10, and the reasons are as follows: Under acidic or neutral conditions, ozone directly attacks organic matter by its molecular form, and the molecular ozone has a high selectivity, which only reacts with the unsaturated aromatic compounds or some certain special groups. However, in the case of alkalinity condition, ozone produces hydroxyl radicals ($\bullet\text{OH}$), which has a stronger oxidation ability and enhances COD removal efficiency [3].

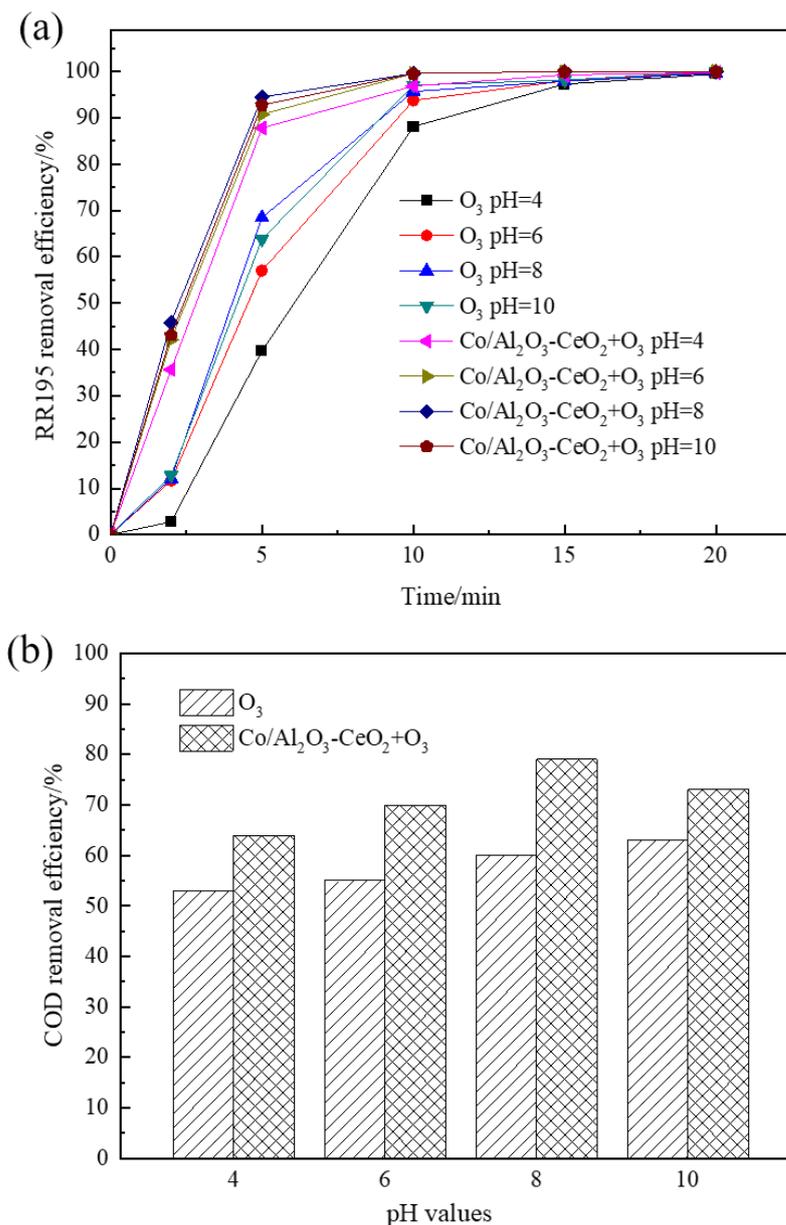


Figure 5. Effect of solution pH on removal of RR195 (a) and COD (b) in the single ozonation and catalytic ozonation (gas flow 200 mL/min, ozone flow 6 mg/min, catalyst dosage 3 g/L, RR195 concentration 400 mg/L, magnetic stirring speed 1400 rpm).

Under catalytic ozonation, the RR195 and the COD removal efficiency increased when pH increased from 4 to 8 and then decreased with a further increase to 10. Due to the acceleration of the ozone decomposition rate with increasing pH from 4 to 8, RR 195 and

COD removal efficiency improved. This, in turn, leads to the formation of the highly reactive radical of $\bullet\text{OH}$ [30], which is beneficial to catalytic ozonation. Other research also found that a higher pH resulted in the formation of stronger oxidative radicals of $\bullet\text{OH}$ [31]. $\bullet\text{OH}$ are mainly generated at alkalinity conditions (pH above 10). Thus, in the single ozonation process, the COD and RR195 removal efficiency reaching the highest value at pH 10 can be explained by the formation of radical species other than hydroxyls. However, under catalytic ozonation, the maximum COD and RR195 removal obtained at pH of 8 may be explained by the fact that the Co/Al₂O₃-CeO₂ can reduce the optimum pH for hydroxyl radical generation. It also can be further inferred that the Co/Al₂O₃-CeO₂ effectively catalyzes ozone decomposition and accelerates oxidative radical formation, resulting in an increased oxidation rate.

It has been reported that the enhancement of catalytic ozonation involves the adsorption of ozone or pollutant or both of them on the catalyst surface, leading to the formation of free radicals, which react with non-adsorbed species in the bulk liquid. Therefore, the surface characteristics of the catalyst play an important role in the oxidation [32]. Solution pH is one of the most important factors affecting oxide surface properties. According to previous studies, the hydroxyl group on the surface of the metal oxides is thought to be the active site providing the catalytic effect and has zero charge when the solution pH is close to the pH_{pzc} of the catalyst. The surface hydroxyl group with zero charge may be the site for catalytic ozone decomposition and for catalytic ozonation of organic compounds [33]. It can be seen that, in the catalytic ozonation process, the COD removal efficiency reached a maximum value when pH was 8, which is very close to the pH_{pzc} of the Co/Al₂O₃-CeO₂ (about 8.45, seen in Figure S2). At that point, the hydroxyl group on the Co/Al₂O₃-CeO₂ surface with zero charge is conducive to catalytic ozone decomposition and catalytic ozonation of RR195. When increasing pH to 10, the strong alkaline condition may affect the density of the surface hydroxyl groups, which causes the loss of the catalytic activity [33]. Therefore, in the catalytic ozonation process, the highest color, and COD removal efficiencies of RR195 are reached at pH 8.

3.6. Stability of the Catalyst

From a practical point of view, an important characteristic of a catalyst is its deactivation or potential reuse. To evaluate the stability of the Co/Al₂O₃-CeO₂ catalyst, it was reused four times without any modifications after the catalyzed ozonation. The COD removal efficiency was determined after each experiment, and the results are shown in Figure S3. In the four series of recycling, the COD removal efficiencies of RR195 were 78.4%, 75.3%, 75%, and 74.8%, respectively. The catalytic activity decreases slightly, which demonstrates that the Co/Al₂O₃-CeO₂ catalyst is effective and stable in the catalytic ozonation of RR195.

3.7. Mechanism of RR195 Degradation

According to Wang and Chen [34], the adsorption of organic molecule on the catalyst is critical for catalytic ozonation. Yuan et al. [35] also found that the adsorption of organics onto the catalyst was an important step which would have a direct influence on the effectiveness of the heterogeneous catalytic oxidation. Therefore, the adsorption capacity of the catalyst needs to be analyzed. Figure 6 shows the adsorption of RR195 on the Co/Al₂O₃-CeO₂ catalyst at pH 8. From Figure 6, it can be seen that, after 20 min, 4.35% of the RR 195 was adsorbed by the Co/Al₂O₃-CeO₂. However, the removal efficiency of RR 195 was 99.8% by catalytic ozonation. This result indicates that adsorption of RR195 on the catalyst's surface occurs, even though it is not obvious when compared with the removal efficiency by the catalytic ozonation process. From the discussion above, it can be assumed that the mechanisms of catalytic ozonation by Co/Al₂O₃-CeO₂ may involve two steps. One is the adsorption of ozone over the catalyst with the formation of hydroxyl radicals, which will react with the pollutants. The other is the adsorption of the organic

pollutant and reaction with ozone molecule (aqueous or gaseous) or adsorption of both reactants with further surface reaction.

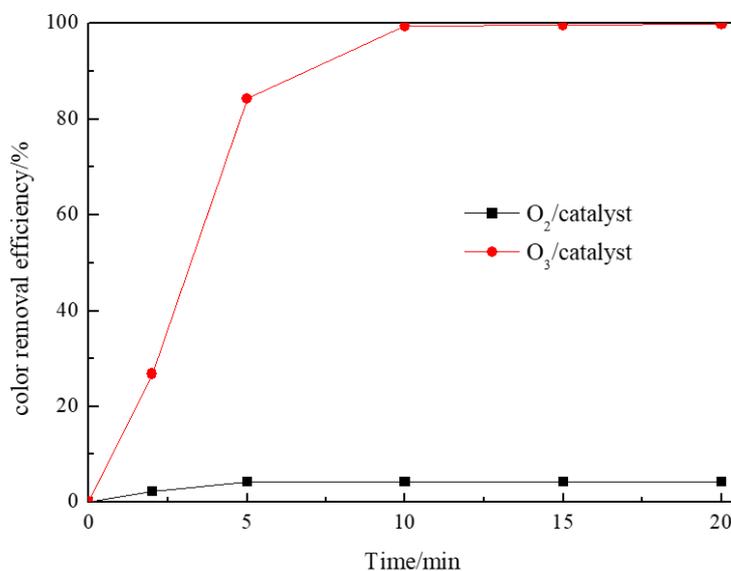


Figure 6. The color removal efficiency of Co/Al₂O₃-CeO₂ adsorption (oxygen gas flow 200 mL/min, RR195 concentration 400 mg/L, magnetic stirring speed 1400 rpm, pH 8) and Co/Al₂O₃-CeO₂ catalytic ozonation processes (gas flow 200 mL/min, ozone flow 6 mg/min, catalyst dosage 3 g/L, RR195 concentration 400 mg/L, magnetic stirring speed 1400 rpm, pH 8).

In order to verify whether the generation of hydroxyl radicals is mainly responsible for the improvement of catalytic ozonation, the influence of radical scavengers was investigated. Tert-butanol (TBA), an organic radical scavenger, was used to indirectly evidence indirectly the transformation of ozone into hydroxyl radicals in Co/Al₂O₃-CeO₂/O₃ process. It has the reaction rate constants of $6 \times 10^8 \text{ M}^{-1}\text{S}^{-1}$ with hydroxyl radicals and $3 \times 10^{-3} \text{ M}^{-1}\text{S}^{-1}$ with ozone, in addition, it cannot be adsorbed on the surface of the catalyst because of its physical-chemical properties [36]. Figure 7 shows the influence of TBA on the degradation of RR195 in catalytic ozonation with Co/Al₂O₃-CeO₂. As illustrated in Figure 7, the presence of TBA inhibited the degradation of RR195 in the Co/Al₂O₃-CeO₂ catalyzed ozonation process, indicating that hydroxyl radicals are formed during the process of Co/Al₂O₃-CeO₂ catalyzed ozonation. The generation of hydroxyl radicals in the Co/Al₂O₃-CeO₂ catalyzed ozonation process may be because the presence of a heterogeneous surface increases the dissolution of ozone and acts as an initiator of the ozone decomposition reaction in the aqueous phase [36]. In addition, a previous study also found that the interaction of ozone with the metal oxide surface results in the formation of free radicals, which can initiate a radical chain-type reaction both on the surface of the catalyst and in the liquid phase [37], the hydroxyl radicals may also be produced through this reaction. However, the removal efficiency of the catalytic ozonation in the presence of TBA was still higher than that of the single ozonation, which implies the existence of another reaction pathway: O₃ directly oxidation of RR 195 after both of them are adsorbed on the catalyst.

The catalytic ozonation of organic compounds involves a number of complex reactions. From the discussion above, it can be assumed that, in Co/Al₂O₃-CeO₂ catalytic ozonation, both surface and liquid bulk reactions occur, involving ozone and •OH radicals. In order to fractionate the contribution of the ozone molecule (δO_3) and hydroxyl radicals ($\delta\cdot\text{OH}$) in the degradation of RR195, kinetic constants were studied and compared between the catalytic ozonation with and without the presence of TBA. This can be described by a simplified and unbalanced reaction mechanism as follows [38]:

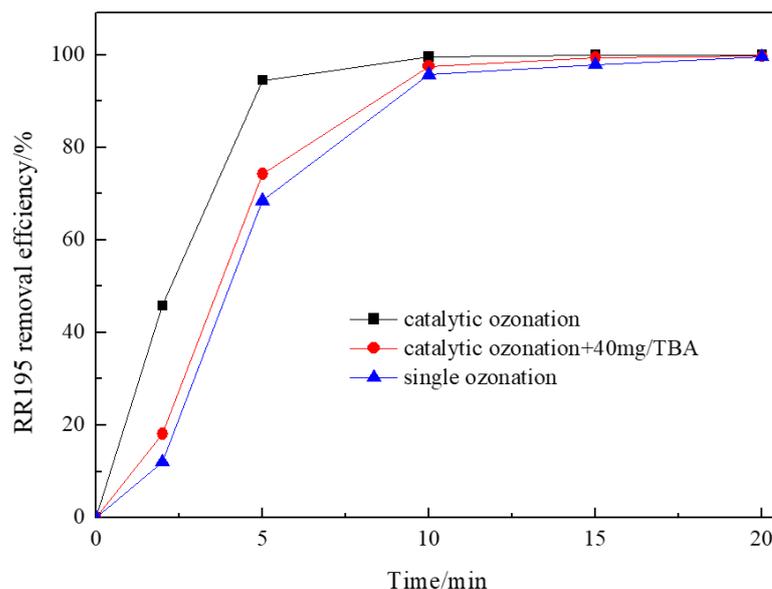
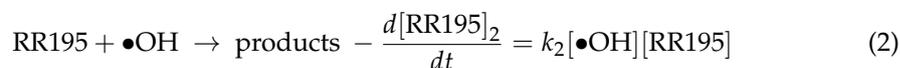
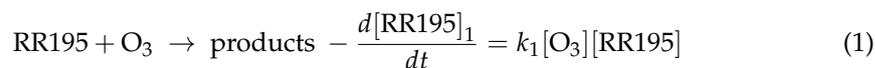
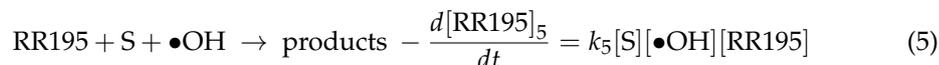
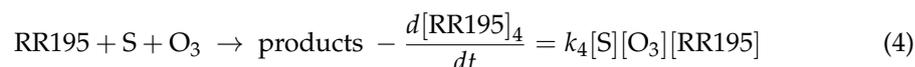
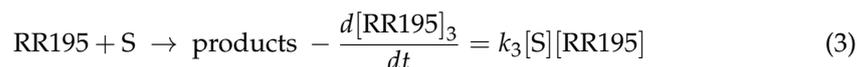


Figure 7. Effect of tert-butanol on ozonation and Co/Al₂O₃-CeO₂ catalytic ozonation processes (gas flow 200 mL/min, ozone flow 6 mg/min, catalyst dosage 3 g/L, RR195 concentration 400 mg/L, magnetic stirring speed 1400 rpm, pH 8).

Homogeneous reactions:



Heterogeneous reactions:



where k_1 and k_2 represent the rate constants of RR195 in homogeneous reaction with molecular ozone and $\bullet\text{OH}$, respectively, $\text{M}^{-1}\text{min}^{-1}$, k_3 represents the adsorption reaction constant between RR195 and the catalyst surface, $\text{M}^{-1}\text{min}^{-1}$, k_4 and k_5 represent the rate constants of RR195 in heterogeneous reaction with molecular ozone and $\bullet\text{OH}$, respectively, $\text{M}^{-1}\text{min}^{-1}$.

Then, the overall RR195 ozonation rate in the presence of Co/Al₂O₃-CeO₂ could be expressed as a sum of (1)–(5):

$$-\frac{d[\text{RR195}]}{dt} = \{k_1[\text{O}_3] + k_2[\bullet\text{OH}] + k_3[\text{S}] + k_4[\text{O}_3][\text{S}] + k_5[\bullet\text{OH}][\text{S}]\}[\text{RR195}] = k_{\text{overall}}[\text{RR195}] \quad (6)$$

where the reactions of the ozonation and catalytic ozonation are expressed with an apparent first-order kinetics constant k_{overall} : $k_{\text{overall}} = k_1[\text{O}_3] + k_2[\bullet\text{OH}]$, $\text{M}^{-1}\text{min}^{-1}$.

According to Equation (6), k_{overall} can be obtained from the slope of $\ln([\text{RR195}]/[\text{RR195}]_0)$ vs. reaction time. When enough inhibitors ([TBA] = 50 mg/L in this study) are introduced

into the catalytic reaction system, the reaction referring to the $\bullet\text{OH}$ oxidation (indirect oxidation) will be terminated. The reaction kinetic after the addition of TBA to the catalytic process can be described in the following equation:

$$-\frac{d[\text{RR195}]}{dt} = k_{\text{TBA}}[\text{RR195}] \quad (7)$$

The fraction of $\bullet\text{OH}$ (δ_{OH}) contributing to the depletion of RR195 can be quantitatively determined by Equation (8):

$$\delta_{\bullet\text{OH}} = 1 - \delta_{\text{O}_3} = \left(1 - \frac{k_{\text{TBA}}}{k_{\text{overall}}}\right) \times 100\% \quad (8)$$

k_{overall} and k_{TBA} were calculated by the plots of $\ln([\text{RR195}]/[\text{RR195}]_0)$ versus reaction time (Figure 8). k_{TBA} was found to be 0.277 min^{-1} , and k_{overall} was 0.5339 min^{-1} , which makes $\delta_{\text{OH}} = 48.7\%$, indicating that $\bullet\text{OH}$ play an important role in the oxidation.

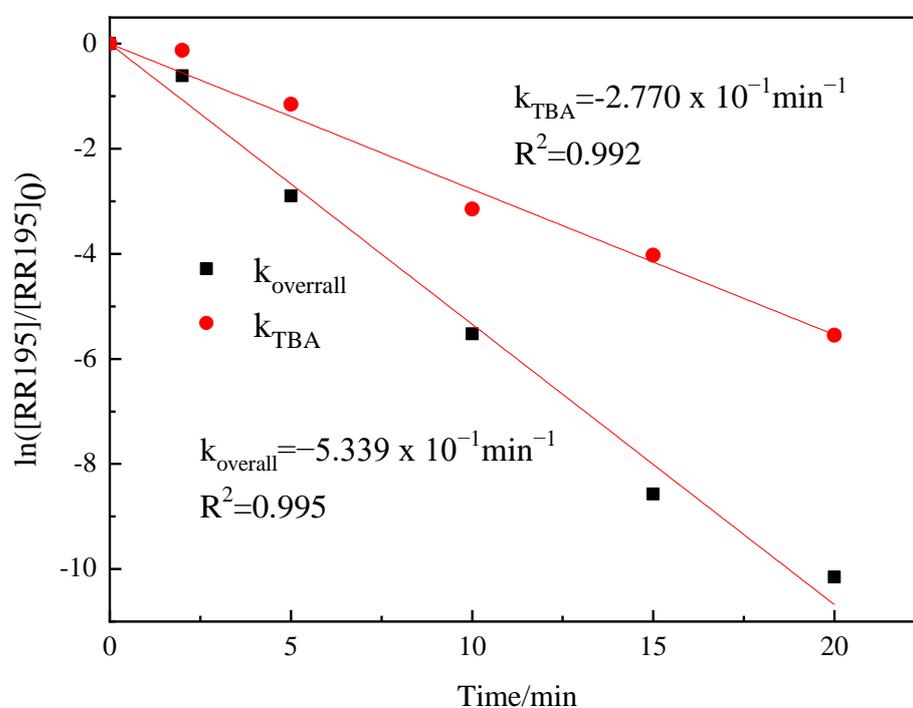


Figure 8. Pseudo-first-order plots of RR195 by catalytic ozonation and catalytic ozonation + TBA (gas flow 200 mL/min, ozone flow 6 mg/min, catalyst dosage 3 g/L, RR195 concentration 400 mg/L, magnetic stirring speed 1400 rpm, pH 8).

From the above experiments, it can be found that the ozonation of RR195 catalyzed by cerium oxide is almost completely inhibited in the presence of TBA, which confirms that hydroxyl radicals play an important role in the reaction mechanism. However, adsorption of RR195 on the catalysts was observed, and it can be accepted as one of the reaction mechanism steps. The possible mechanism of catalytic ozonation includes an indirect oxidative reaction by hydroxyl radicals and a direct oxidation reaction by O_3 after the ozone and RR195 adsorbed on the surface of the catalyst (Figure 9).

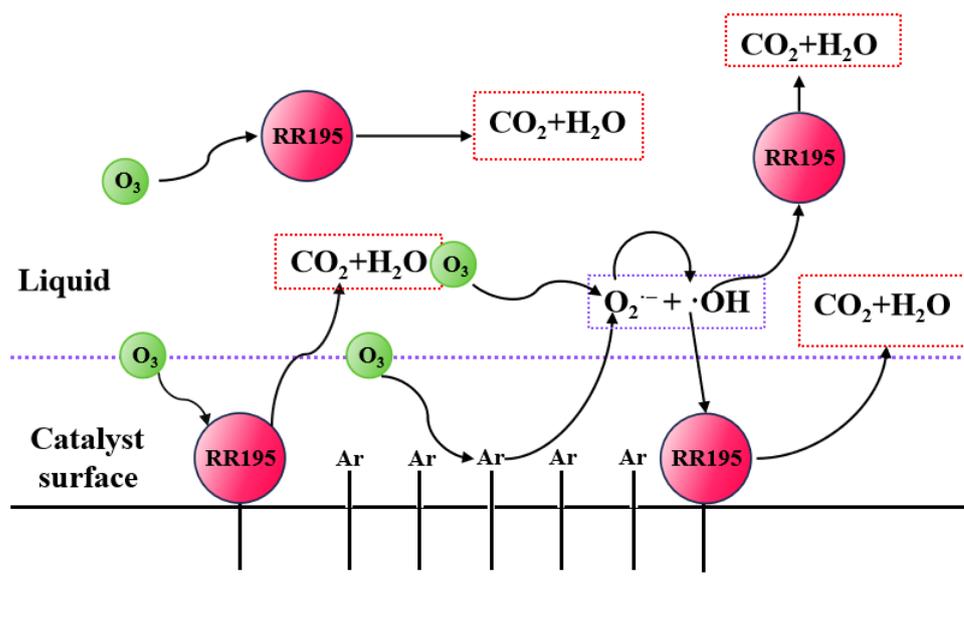


Figure 9. Mechanism of catalytic ozonation RR195.

4. Conclusions

This study shows that the Co/Al₂O₃-CeO₂ catalyst is efficient in the catalytic ozonation of RR 195 solution, and it accelerates the color and COD removal more in comparison with single ozonation. The optimum pH was determined to be 8, and the optimum catalyst dosage was 3 g/L. The RR 195 removal efficiency decreased with increasing RR 195 concentrations from 200 to 800 mg/L. The Co/Al₂O₃-CeO₂ catalyst had good stability after four successive recycles. The amount of RR 195 adsorbed by Co/Al₂O₃-CeO₂, which was negligible compared with the removal rate of the catalytic ozonation process. The presence of TBA was shown to inhibit the degradation of RR 195 by Co/Al₂O₃-CeO₂ catalytic ozonation. The experimental results indicate that the possible mechanism of catalytic ozonation includes an indirect oxidative reaction by hydroxyl radicals and a direct oxidation reaction after the ozone and RR195 adsorbed on the surface of the catalyst.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr11072141/s1>, Figure S1. The particle size distribution of the catalyst. Figure S2. The pHPZC value of catalyst. Figure S3. The effect of catalyst recycle times on the ozonation of RR 195. (RR 195 concentration 400 mg/L, catalyst dosage 3 g/L, gas flow 200 mL/min, ozone flow 15 mg/min, pH 8, reaction time 20 min).

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