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Alkaline Prehydrolysis Prolongs Resin Life and Enhances the Adsorption of Phenolic Compounds

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Abstract: Phenolic compounds in oil wastewater are highly toxic and refractory. Hydrolysis at pH 12 for 12 h makes these compounds more vulnerable to attack and destruction. Under the binding and precipitation of polyaluminum chloride (PAC) at pH 8, the chemical oxygen demand (COD) was significantly reduced by 38%. The simulation found that hydrolysis + flocculation was a complex multistep process. The COD removal rate was mainly controlled by the prehydrolysis process. The metabolic pathway suggested that the m-cresol produced in the factory was oxidized to low water-soluble aldehyde. Alkaline hydrolysis converted the aldehyde into m-toluene-methanol, which was conducive to being captured by the PAC. Fourier transform infrared spectroscopy (FTIR) showed that the alkaline dehydrogenation of two m-methylphenyl carbinols produced a molecule that was removed by the resin. Generally, the particle size of the residue after alkaline hydrolysis was 6.4–8.3 nm, which was included in the pore size range of the resin. Therefore, the resin adsorption capacity for the hydrolyzed substances increased to 47,000 mg L^{-1}, with 93% renewability. In short, hybrid technology reduces the concentration burden of the resin inflow and controls the molecular size of adsorbed substances for repurification. It strengthens the treatment effect of high COD wastewater and provides innovative ideas for extending the service life of resin.

Keywords: prehydrolysis; phenolic compounds; resin sorption; particle size; renewable

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1. Introduction

Phenolic compounds are prototype toxic substances. Butylated hydroxytoluene (BHT) and its derivatives are common highly toxic and refractory organic compounds in petrochemical wastewater. Phenolic substances in wastewater mainly include phenol, cresol, and 6-tert-Butyl-m-cresol, which originate from petroleum, petrochemical, coal chemical, phenol, and phenolic resin production [1]. For each ton of phenolic resin production, 750 L of wastewater containing 600–42,000 mgL^{-1} of phenol needs to be discharged [2]. Phenolic compounds are toxic to biological individuals and can enter the human body through respiration and skin contact, causing teratogenesis and carcinogenesis. Various countries have successively listed phenolic compounds as the priority pollutants in water control [3].

The commonly used methods for treating phenol-containing wastewater include biochemical methods [1,4], advanced oxidation, electrochemical methods [5], and adsorption [1]. However, phenolic compounds exceeding a concentration of 1000 mgL^{-1} will inhibit the biotreatment capacity of the bioreactor [6]. The intermediates of BHT degradation, such as BHT-Q and BHT-tert-butanol, are more toxic than BHT; therefore, their concentration will increase compared with the influent [7]. Fenton, photoelectric Fenton, electro-Fenton, and other oxidation methods have obvious treatment effects; however, they are difficult to control due to their high energy consumption and harsh reaction conditions [8]. Resin adsorption has the advantages of treating high concentrations with no secondary pollution and regenerating valuable substances. However, desorption treatment is required after adsorption saturation; therefore, it is necessary to reduce the feed concentration of the resin, and the molecular size of the adsorbed resin is required to facilitate its desorption. In the case of alkaline prehydrolysis, it loosens the phenolic structures, breaking the C-O bonds [9], and promotes the generation of hydroxyl radicals in the advanced oxidation process [10], which effectively removes the phenolics [11]. In practice, it is difficult for a single technology to economically and effectively treat wastewater to meet the standard; therefore, it is imperative to develop a combined process.

To prolong the service life of the resin, it is necessary to identify methods to strengthen its adsorption and desorption; therefore, alkaline hydrolysis was used to pretreat the pollutants. Referring to the effect of the advanced oxidation of phenolic compounds, the present study focused on the process of reducing the content of the phenolic compounds and breaking their molecular structure by alkaline prehydrolysis. The pathways of substance decomposition by advanced oxidation and alkaline hydrolysis were investigated separately using liquid chromatography–mass spectrometry (LC–MS). Fourier transform infrared spectroscopy (FTIR) was used to study the effect of the alkaline hydrolysis on the surface functional groups of the flocs and their ability to capture the phenol. Finally, based on the molecular weight obtained from the alkaline hydrolysis of the substance, the effect of the product size on the adsorption and desorption times of the resin was analyzed, and its service life was estimated. The present study provides a case for the establishment of an alkaline pretreatment scheme for high chemical oxygen demand (COD) wastewater and the recovery of effective substances.

2. Materials and Methods

2.1. Materials

Baotashan New Materials Co., Ltd. (Xianyang, China) generates 3 m^3 phenolic wastewater per day. Its pH is between 9 and 10, and the COD is 140,000 mgL^{-1}. The wastewater contains large molecules of phenols that are difficult to volatize. The aim was to discharge water that met the Integrated Wastewater Discharge Standard (GB8978-1996), with a COD of <500 mgL^{-1}.

2.2. Methods

2.2.1. Alkaline Prehydrolysis Experiment

Wastewater (100 mL) was used for the alkaline hydrolysis experiment. (1) After adding 10 mL of 1200 mgL^{-1} polyaluminum chloride (PAC) to the wastewater, it flocculated and settled for 12 h, and the COD of the supernatant was measured as a control. (2) The wastewater was hydrolyzed at pH 12 for 12 h; then, 10 mL of 1200 mgL^{-1} PAC was added to the mixture, which was flocculated and precipitated for 12 h, and the COD of the supernatant was measured. (3) The wastewater was hydrolyzed at pH 12 for 12 h; then, it was flocculated and precipitated for 12 h after adding 10 mL of 1200 mgL^{-1} PAC, after which its pH was adjusted to 8, and the COD of its supernatant was measured. (4) The wastewater was hydrolyzed at pH 12 for 4, 6, 8, 10, 12, and 24 h, after which its pH was adjusted to 8. Next, it was flocculated and precipitated for 12 h after adding 10 mL of 1200 mgL^{-1} PAC; then, the COD of its supernatant was measured.

2.2.2. Macroporous Resin Adsorption Experiment

The macroporous resin (XDA-1G, Sunresin New Materials Co., Ltd., Xi'an, China) was pretreated with 100 mL of anhydrous ethanol to fill the column. The column was washed with 2–3 times the volume of water until there was no alcohol odor at the outlet. The initial 80 mL effluent was discharged as waste; then, its COD was measured, and LC–MS (8050CL) and FTIR (FTIR-650) were carried out.

The measurement parameters of the LC–MS were as follows: ion source ESI (electron spray ionization) (negative), drying gas (temperature 325 °C, flow rate 10 L min^{-1}), atomization pressure 50 psi, capillary voltage 4000 V, and mass spectrometry scan range (m/z) 50~500.

The measurement parameters of the FTIR were as follows: spectral range (4000–400 cm^{-1}), resolution (0.1–0.5 cm^{-1}), light range (2–10 cm), and scanning speed (1–20 cm/s).

2.2.3. Regeneration Life Test of the Macroporous Resin Adsorption–Desorption

Wastewater (100 mL) flowed through the packed column at a rate of 0.1 L min^{-1}. After the adsorption test, the column was backwashed with heated 4% NaOH solution. Subsequently, the column was flushed with 2–3 times the volume of water for desorption and to remove the residual alcohol in the resin. The regeneration capacity of the macroporous resin was determined based on the COD of the effluent after desorption.

2.2.4. Liquid Chromatography–Mass Spectrometry (LC–MS) Detection

The effluent samples were collected and analyzed using LC–MS. The parameters used were ion source ESI (electron spray ionization) (negative), drying gas (temperature of 325 °C, flow rate of 10 L min^{-1}), atomization air pressure of 50 psi, capillary voltage of 4000 V, and mass spectrometry (MS) scan range (m/z) of 50 to 500.

The simulations used pseudo-first-order, pseudo-second-order, Elovich kinetic, and intra-particle diffusion models.

The effect of the alkaline hydrolysis on the degradation of the phenolic substances was investigated using the pseudo-first-order, pseudo-second-order, and Elovich kinetic models, and the equation for intra-particle diffusion. The simulation curve was drawn with Origin software (9.0).

Pseudo-first-order kinetic model:

$$\ln(Q_e - Q_t) = -k_1 t + \ln Q_e \tag{1}$$

Pseudo-second-order kinetic model:

$$t/Q_t = t/Q_e + 1/\left(k_2 {Q_e}^2\right) \tag{2}$$

Elovich kinetic model:

$$Q_t = (1/\beta)\ln t + (1/\beta)\ln(\alpha\beta) \tag{3}$$

The equation for intra-particle diffusion:

$$Q_t = k_3 t^{1/2} \tag{4}$$

where Q_e and Q_t refer to the amount of COD removed at equilibrium and at any time t (h), respectively; k_1, k_2, β, and k_3 are the rate constants for the pseudo-first-order kinetic, pseudo-second-order kinetic, Elovich kinetic, and intra-particle diffusion models, respectively, in units of $L \cdot min^{-1}$, $g \cdot mg^{-1} \cdot min^{-1}$, $L \cdot min^{-1}$, and $mg \cdot g^{-1} \cdot min^{-1}$, respectively, for the reaction process; α is the parameter for the initial reaction rate of the Elovich kinetic equation, $mg \cdot g^{-1} \cdot min^{-1}$; and β is the Elovich kinetic equation constant, $mg \cdot g^{-1}$.

Each data point was measured in triplicate.

3. Results

3.1. Effect of the Hydrolysis pH on the Flocculation and Phenol Removal

The COD of the raw water was 100,000 mgL^{-1}, and the pH was between 8 and 10. As shown in Figure 1, when the PAC was added directly, the residual COD after flocculation reached 80,000 mgL^{-1}. After 12 h of alkaline hydrolysis at pH 12, the PAC was added to the wastewater, and the COD of the supernatant after flocculation decreased to 68,000 mgL^{-1}. After hydrolysis, the pH was adjusted to 8, and the COD of the supernatant after flocculation was 62,000 mgL^{-1}, which was significantly lower than the previous result. After alkaline hydrolysis of the phenol-containing wastewater, the PAC was first added for flocculation, and then the pH was adjusted to 8. The COD in the supernatant was 66,400 mgL^{-1}. This result was between the treatment effects of the two abovementioned methods.

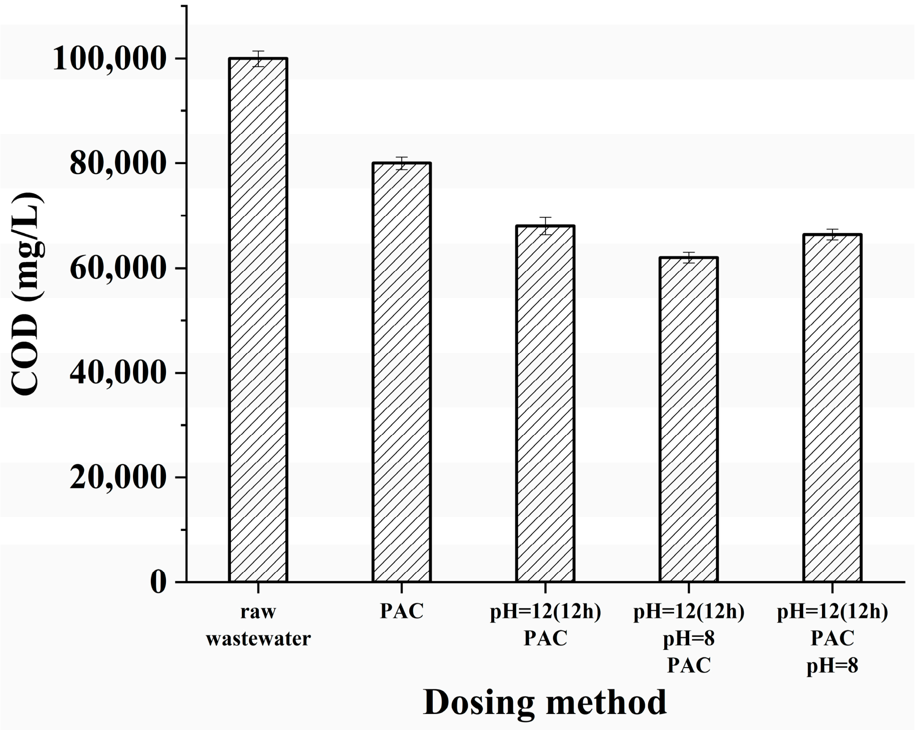

Figure 1. Effect of the hydrolysis pH on the COD removal by flocculation.

Therefore, alkaline hydrolysis was necessary for the pretreatment of the phenolic wastewater. This was because the phenol structure in the wastewater loosened, and the C-O bond gradually broke due to the catalysis of the alkaline reagents [11,12]. Macromolecular phenolic substances were disassembled into small molecules, which were then wrapped and precipitated by the PAC and removed as precipitates, resulting in a substantial decrease in the COD. After the alkaline hydrolysis, the wastewater pH was adjusted to 8, which resulted in the best flocculation performance of the PAC. This was because the PAC was hydrolyzed to stable and strongly bridged Al_{13} at pH 8 [13]. When the pH was 12, the hydrolytic precipitation of the PAC was converted into soluble ions, such as AlO_2, with poor electric neutralization and sweep ability. This led to a poor flocculation effect [14]. In addition, different pH values led to different forms of phenolic compounds, which led to different reaction processes. Most phenolics are hydrophilic and have a constant to measure the degree of acid–base dissociation. When the wastewater pH is too high and greater than this constant, the phenolic substances are in ionic form [5]. However, the phenolic compounds were more vulnerable to be attacked by alkaline reagents when they existed in molecular form, causing their structure to be destroyed. Finally, after hydrolysis and flocculation, the effect of the pH adjustment on the COD reduction was not obvious. This was because the PAC formed a more stable structure with the phenolic substances and their derivatives (Section 3.3); therefore, it did not participate in the subsequent reaction at pH 8.

3.2. Effect of the Alkaline Hydrolysis Time on the COD Removal

The effect of the hydrolysis time on the COD removal of the wastewater was studied, and the results are shown in Figure 2A. The initial COD reached 100,000 mgL^{-1}, and the residue COD was reduced to 47,000 mgL^{-1} after 24 h, with a 53% removal efficiency. With increasing time, the COD significantly decreased from 56,000 to 48,800 mg L^{-1} within 4–8 h, and the cumulative removal efficiency rapidly increased from 44% to 51.2%. With increasing hydrolysis time, the C-O and O-O bonds of the hydroxyl groups were broken more completely, as the alkaline reagent and the phenolics in the wastewater came into full contact [12]. In this case, more macromolecules were broken into smaller macromolecules, resulting in a significant decrease in the COD. However, when the alkaline hydrolysis exceeded a duration of 12 h, the COD slightly decreased from 47,200 to 47,000 mgL^{-1}, and the COD removal efficiency curve gradually flattened to 52.9–53%. The results showed that the system reached equilibrium after 12 h, and the removal of the COD by hydrolysis did not only depend on hydrolysis time. All the original phenolic substances in the wastewater were destroyed in the structure, the C-O and O-O bonds were completely broken, and the disassembled substances combined with the PAC to form new substances with a stable structure. Therefore, the residual COD did not decrease significantly, and there was almost no increase in the cumulative removal efficiency.

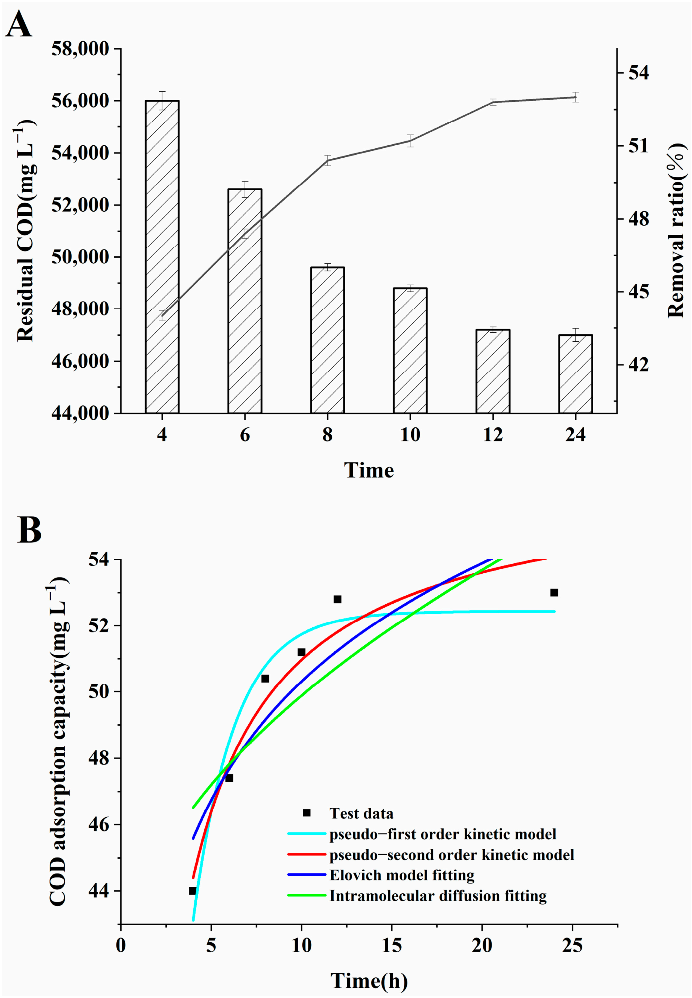

Figure 2. Effect of the alkali hydrolysis time on the COD removal (**A**) and its fitting curve (**B**).

In contrast to the oxidation methods for the treatment of phenol-containing wastewater [15,16], alkaline hydrolysis uses only alkaline reagents and facilitates the extraction and recovery of useful substances from the intermediate products obtained from the treatment. In contrast to hydrolytic acidification, the phenolic wastewater is hydrolyzed from insoluble organic matter to soluble material by the action of a large number of hydrolytic bacteria, which converts insoluble substances into easily biodegradable ones, both of which are released into the mixture, so that the COD concentration of the reactor effluent is still very high, with a COD removal rate of only 30% [17]. However, the alkaline reagent of alkaline hydrolysis acts directly on the C-O bond of the phenols, resulting in an increase in the COD removal of up to 50%.

Notably, because the hydrolysis time was related to the molecular size of the phenols, and the molecular size of phenols was related to the removal effect of the PAC adsorption, the hydrolysis time was indirectly related to the PAC adsorption. Therefore, an adsorption kinetic model was used for fitting. With increasing alkaline hydrolysis time, the decline in the COD in the water was simulated using pseudo-first order, pseudo-second order, Elovich kinetic, and intra-particle diffusion models, as shown in Figure 2B; the fitting parameters are listed in Table 1.

Table 1. Kinetic parameters.

Models	Parameters	
Pseudo-first-order kinetic model	K_1 R^2	0.432 0.93453
Pseudo-second-order dynamics model	K_2 R^2	0.01616 0.93947
Elovich kinetic model	α β R^2	8891.15855 0.1939 0.78161
Intra-particle diffusion model	K_3 R^2	2.90067 0.6252

Table 1 shows that the R^2 values of the alkaline hydrolysis in the four kinetic models were 0.93453, 0.93947, 0.78161, and 0.6252, and both the pseudo-first-order and pseudo-second-order kinetic models were applicable. However, the R^2 value of the pseudo-second-order dynamics model was higher than that of the pseudo-first-order kinetic model, indicating that the alkaline hydrolysis process was most consistent with the proposed secondary kinetic model, and the reaction rate was mainly controlled by the chemical reaction. The pseudo-first-order kinetic model was generally suitable for faster rate reaction processes, while the pseudo-second-order dynamics model was more suitable for complex multistep reaction processes [18,19]. This showed that the alkaline hydrolysis of this phenol-containing wastewater was a complex multistep process.

3.3. The Putative Metabolism Pathway of the BHT

Based on the known main production reaction of the factory, it was speculated that the abundant substances present in the initial wastewater were 2,6-di-tert-butyl-4-methylphenol (BHT) (220.35), 4,6-di-tert-butyl-m-cresol (220.35), and m-cresol (108.14). The substances obtained after different treatments are shown in Table 2. The m-cresol was prone to oxidize to 3-methylbenzaldehyde by O_2 at 25 °C and standard pressure [20]. The Gibbs free energy of the reaction was −32.69 KJ, which indicated that it could occur spontaneously at room temperature and standard pressure. Therefore, 3−methylbenzaldehyde (120.15) could replace m−cresol when the wastewater was stored in the collector for a long time.

Table 2. The composition of the raw sewage and after different treatments.

Different Treatments	Composition
Raw wastewater	m-cresol; 3-methylbenzaldehyde
Alkaline hydrolysis	m-tolylmethanol
Alkaline hydrolysis + PAC	3-hydroxy-5-methylbenzyl chloride; 1-methyl-3-[(3-methylphenyl) methylperoxymethyl]benzene
Alkaline hydrolysis + PAC + resin adsorption	6-{[3,5-bis(tert-butyl)-4-hydroxyphenyl]methyl}-2-(tert-butyl)-4-chlorophenol

Figure 3 shows the changes in the residual substances detected in the wastewater after the successive treatment of the alkaline hydrolysis, the PAC flocculation–sedimentation, and the resin adsorption. 3-Methylbenzaldehyde can undergo the Cannizzaro reaction to form m-tolylmethanol (122.17), which requires adjusting the wastewater to a strong alkaline condition [21]. When the PAC was added, it was hydrolyzed to produce HCl, which replaced the methane H in water to produce dichloromethane [22]. The dichloromethane and m-tolylmethanol underwent Fourier alkylation in the alkaline environment in which $AlCl_3$ existed [23], and the H on the benzene ring was replaced to form 3-hydroxy-5-methylbenzyl chloride (156.61). Meanwhile, two molecules of m-tolylmethanol formed 1-methyl-3-[(3-methylphenyl)methylperoxymethyl]benzene (242.31). Both 3-hydroxy-5-methylbenzyl chloride and 1-methyl-3-[(3-methylphenyl) methylperoxymethyl]benzene showed 10^6 levels of strength in the mass spectrum, and neither of these substances was detected after the resin adsorption, indicating that they were removed by the adsorption. The mass spectrum of the resin adsorbed effluent showed that all substances were at a level of 10^6. It was speculated that the tert-butyl group of 4,6-di-tert-butyl-m-cresol in the raw water was replaced by Cl^-, which was generated by the hydrolysis of the PAC [22], after which it reacted with 2,6-di-tert-butyl-4-methylphenol (BHT) to generate 6-{[3,5-bis(tert-butyl)-4-hydroxyphenyl]methyl}-2-(tert-butyl)-4-chlorophenol (403). Its molecule was larger than the pore size of the resin; therefore, it was not absorbed and removed by the resin.

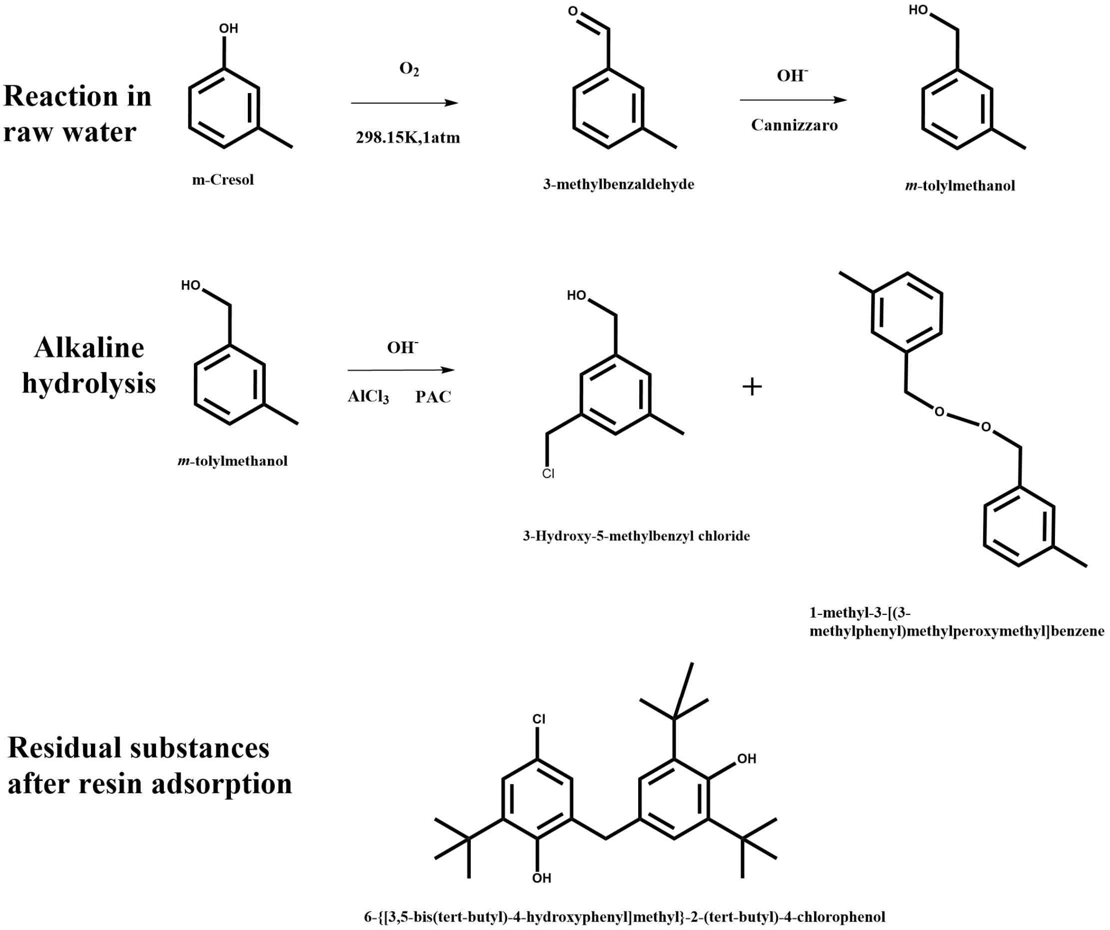

Figure 3. Inferred residual material structure in the wastewater treatment.

In short, although m-cresol was processed and produced by the factory, the real pollutant in the wastewater after exposure to O_2 was a low water-soluble aldehyde. Alkaline hydrolysis was conducive to the conversion of the aldehydes into m-toluene methanol dissolved in water, which was conducive to the water solubility of phenol and its capture by the PAC. Macromolecules that could not be adsorbed by the PAC were also excluded from the pore size of the resin. This reduced the inflow concentration pressure of the resin and assisted in the purification of valuable m-toluene methanol and resin regeneration.

3.4. FTIR Characteristic Analysis of the Functional Groups on the Surface of the Flocs after Hydrolysis

The FTIR spectra of the effluents from the alkaline hydrolysis, pre-oxidation, alkaline hydrolysis + resin adsorption, and pre-oxidation + resin adsorption are shown in Figure 4. The results of the different treatments showed no significant difference between 400 and 1500 cm^{-1}. The peak at 1500–1800 cm^{-1} was the stretching of the carbonyl C=O and the contraction of the benzene ring C=C bond [24,25]. Based on the MS analysis, it was found that the effluent from the four treatments formed similar products, which comprised 3-methylbenzaldehyde and 1-methyl-3-[(3-methylphenyl)methylperoxymethyl]benzene (see Figure 3) and contained numerous C=O bonds. However, the peaks formed by the other three treatments were comparable, except that the alkaline hydrolytic effluent had the lowest absorption peak. This may be because the H on the phenol hydroxyl was easily ionized with alkali to form negative oxygen ions [26]; thereby, the absorption peak shifted to the right, and the absorption intensity weakened.

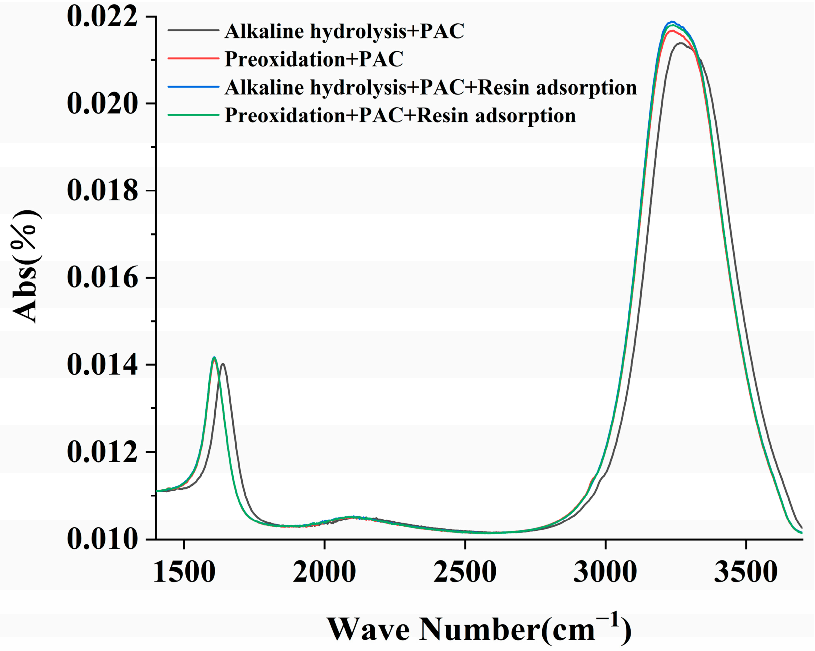

Figure 4. The FTIR characteristics of the wastewater after different treatments.

The peak at 3000–3500 cm^{-1} should be the contraction vibration of OH [27,28]. The order of the peak strength was the alkaline hydrolysis < pre-oxidation < alkaline hydrolysis + resin adsorption < pre-oxidation + resin adsorption. The OH bond vibration without the resin was weaker than that with the resin. This may be due to the alkaline dehydrogenation of two m-tolylmethanol to form a 1-methyl-3-[(3-methylphenyl)methylperoxymethyl]benzene molecule, which was equivalent to the reduction of two phenol hydroxyl molecules [29]. After the resin adsorption, 1-methyl-3-[(3-methylphenyl)methylperoxymethyl]benzene was removed, and only the 6-{[3,5-bis(tert-butyl)-4-hydroxyphenyl]methyl}-2-(tert-butyl)-4-chlorophenol contraction vibration was reflected using the FTIR (see Figure 3).

3.5. Effect of the Prehydrolysis on Improving the Service Life of the Resin Adsorption

The raw water and the alkaline-hydrolyzed wastewater were adsorbed by macroporous resin. Next, the hot lye was backwashed three times for regeneration. The phenol hydroxyl group produced sodium phenol in the alkaline environment, and the adsorption balance between it and the resin adsorption site was broken; therefore, the adsorbed molecules were dissolved back into the water phase [30]. As shown in Figure 5, the removal capacity of the resin to COD in the raw water or alkali-hydrolyzed water decreased with the increasing number of elutions. The two types of wastewater were treated by passing the resin at the same flow rate. After being eluted five times, the adsorption capacity of the resin for the COD in the raw water stabilized at approximately 45,000 mg L^{-1}, which was 89.79% of its initial capacity. However, the adsorption capacity of the resin for the COD in the alkali-hydrolyzed water stabilized at approximately 47,000 mg L^{-1}, reaching 93% of its initial capacity. The regenerated adsorption COD of the resin for the alkali hydrolysis was significantly higher than that of the raw water, and the prehydrolysis prolonged the service life of the resin adsorption.

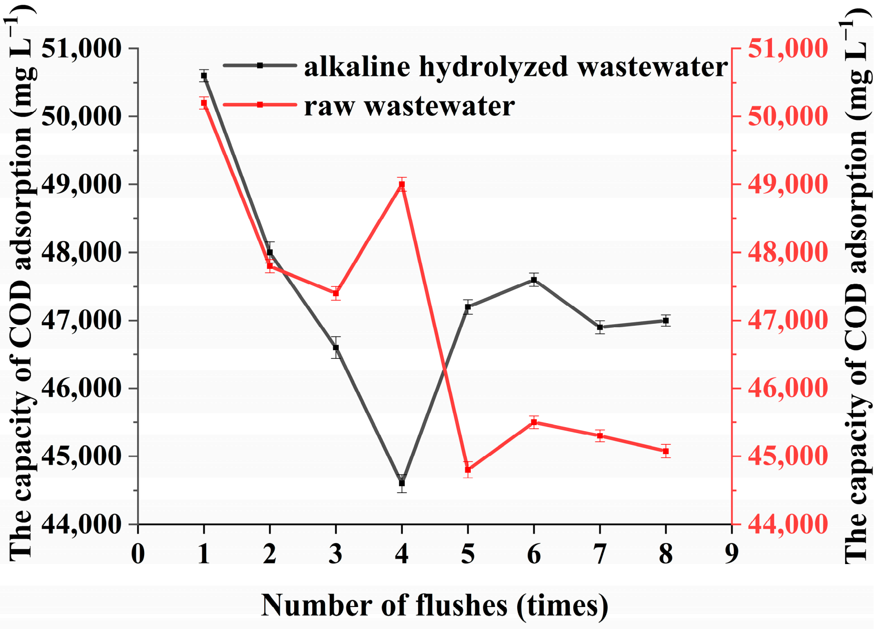

Figure 5. Effect of the prehydrolysis on improving the resin adsorption capacity.

The sizes of the substances obtained from the different treatments are shown in Table 3. The mass spectrum analysis results showed that the alkaline hydrolytic effluent contained [3-(chloromethyl)-5-methylphenyl] methanol and 3,3′-[peroxybis(methylene)]bis(toluene) with diameters of 6.4 and 8.3 nm, respectively (see Figure 3). The raw water contained m-cresol, 4,6-di-tert-butyl-m-cresol, and 2,6-di-tert-butyl-4-methylphenol (BHT) with diameters of 6.3, 8.3, and 8.8 nm, respectively. However, the average pore size of the resin used was fixed at 8.5–9.5 nm. The diameters of the substances in the raw water and the hydrolysis water were smaller than the average pore size of the resin, which proves that they can be captured by the macropores. However, it was assumed from the molecular size that the substances produced by the alkaline hydrolysis were smaller; therefore, the hydrolyzed effluent was more easily adsorbed by the resin to reduce more COD. It was also determined that the resin was more selective in adsorbing organic compounds with smaller molecular sizes. The pore and particle size decreased along with the increase in the number of flushes [31].

Table 3. The molecular size of the substances produced.

Material	Long	Wide	High	Volume	Diameter
m-Cresol	8.653	7.189	4.018	249.95	6.3
4,6-di-tert-butyl-m-cresol	10.752	8.196	6.505	573.24	8.306
2,6-di-tert-butyl-4-methylphenol (BHT)	11.453	8.990	6.505	669.77	8.75
3-Methylbenzaldehyde	9.022	7.316	4.018	265.21	6.424
m-tolylmethanol	8.868	7.736	4.019	275.71	6.508
3-hydroxy-5-methylbenzyl chloride	11.116	8.087	4.019	361.29	8.322
1-methyl-3-[(3-methylphenyl) methylperoxymethyl]benzene	15.773	8.040	4.545	576.37	8.255
6-{[3,5-bis(tert-butyl)-4-hydroxyphenyl]methyl}-2-(tert-butyl)-4-chlorophenol	15.372	10.212	8.312	1304.8	10.928

4. Conclusions

The wastewater produced during petroleum production contains phenolic compounds, which are organic substances that are highly toxic and difficult to degrade. In the present study, a novel technology combined with alkaline hydrolysis and resin adsorption was used to treat phenol-containing wastewater.

The hydrolysis pH was controlled at 12 and maintained for 12 h. Phenolic compounds existed in molecular form. They were more vulnerable to attack and destruction by alkaline reagents. After the pH was adjusted to 8, phenols were wrapped with the PAC and precipitated, resulting in a COD reduction of 38%. With the increase in the hydrolysis time, the COD removal rate increased rapidly from 44% to 51.2%. After 12 h, the COD removal rate gradually stabilized at 52.9–53%. Based on the kinetic model simulation, the hydrolysis + flocculation results were the most consistent with the secondary kinetic model. It was a complex multistep process, and the COD removal rate was mainly controlled by the prehydrolysis. The metabolic pathway revealed that although m-cresol was produced in the factory, it was oxidized to a low water-soluble aldehyde. Alkaline hydrolysis converted aldehydes into m-toluene-methanol, which was conducive to the dissolution of phenol and for capturing the PAC. The FTIR showed that the effluents from the alkali hydrolysis, pre-oxidation, and resin adsorption had similar products, containing numerous C=O bonds. Because the alkaline dehydrogenation of two m-methylphenyl carbinols forms 1-methyl-3-[(3-methylphenyl) methylperoxymethyl] benzene molecules, which were removed by the resin, the OH bond vibration of the remaining substances after the resin adsorption was stronger than that without the resin. The particle size of the material produced by the alkali hydrolysis was 6.4–8.3 nm, which was smaller than that of the raw water (6.3–8.8 nm). The adsorption capacity of the resin for the COD in the raw water was 45,000 mg L^{-1}, with 89.79% renewability, while the adsorption capacity for the alkaline-hydrolyzed water was 47,000 mg L^{-1}, with 93% renewability.

In conclusion, the alkali prehydrolysis before the resin adsorption can enhance the treatment effect of high-COD wastewater, reduce the concentration burden of the resin inflow, facilitate the control of the molecular size of adsorbed substances for repurification, and provide innovative ideas to help resin elution and extend its lifespan.

Author Contributions: C.G.: Conceptualization; Methodology; Supervision; K.Y.: Methodology; Writing—Original Draft; L.B.: Formal analysis; Validation; X.Z.: Data Curation; Investigation; Y.H.: Resources; Project administration; J.F.: Resources; Project administration; J.Q.: Resources; Project administration. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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