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Degradation of Coke Plant Wastewater by Supercritical Water Oxidation

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The wastewater of coke plant was treated by using supercritical water oxidation process. The effects of H_2O_2 excess multiple, reaction temperature, pressure and residence time were investigated. The experimental results showed that the reaction temperature is the main factors which affect the removal of coke plant wastewater. The suitable conditions of the degradation of coke plant wastewater were ascertained. With the multiples of oxygen in excess of 1.6, the temperature 520-550 ºC, the pressure 27-28 MPa and the residence time over 2 min, the removal rate of COD_{Cr} was up to 99 %.

Key Words: Supercritical water oxidation, Coke plant wastewater, Removal rate.

INTRODUCTION

Coke plant wastewater is kind of intractable waste water which is from the process of high-temperature carbonization of coal, purifying coal gas and chemical products purification. Components of coke plant wastewater are complex, which contain phenol, polycyclic aromatic hydrocarbons and oxygen, sulphur, nitrogen heterocyclic compounds and coke plant wastewater is difficult to treat. The general process of dealing with coke plant wastewater has to go through pre-coking, secondary treatment and advanced treatment before meeting the discharge standards. In short, the coke plant wastewater pollution is a serious environmental issue[1,2]. Supercritical water oxidation (SCWO) has attracted the attention of environmental workers for its efficient and environmentally friendly features, especially when dealing with difficult degradation of organic matter with unparalleled advantages over other conventional treatment methods, removal rate of organic is high (typically greater than 99 %) and complete and the final decomposition is CO_2, H_2O, N_2 and other environmentally friendly substances[3,4]. Supercritical water oxidation reaction is homogeneous reaction with rapid reaction speed of less than 2 min remaining time and treatment efficiency is high[5-7]. In the present work, coke plant wastewater was treated by using supercritical water oxidation process. The effects of H_2O_2 excess multiple, reaction temperature, pressure and residence time were investigated, providing the basis for the application of supercritical water oxidation in coke plant wastewater treatment.

EXPERIMENTAL

The original coke plant wastewater was obtained form chemical plant in Shanxi of China, the initial COD_{Cr} of coke plant wastewater is 7295 mg/L. H_2O_2 was used as the oxidizing agent. Research grade reagents used during Chemical Reagent Development Center (China).

The flow chart of supercritical water oxidation system was given in Fig. 1.

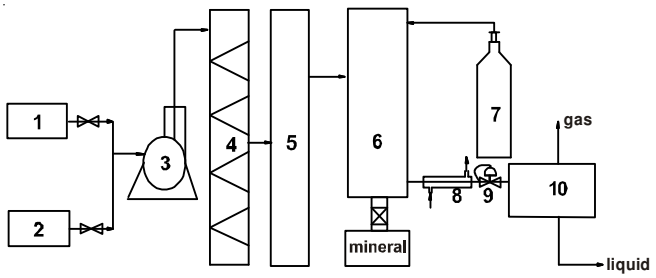

Fig. 1. Flow chart of supercritical water oxidation system 1. Wastewater feed tank; 2. H_2O_2 feed tank; 3. High pressure compressor; 4. Liquid pre-heater; 5. Mineral-water separator; 6. Reactor; 7. Cooler; 8. High-pressure cylinder; 9. Back pressure regulator ; 10. Gas-liquid separator

Analytical methods: The COD analysis was performed by the dichromate closed reflux method (GB 1941-1989, China).

RESULTS AND DISCUSSION

Effect of oxygen excess: The oxygen excess was calculated over the theoretical amount of oxygen required for complete

oxidation. In the experiments the oxygen dosage could be referred to as the stoichiometric weight ratio between the oxygen and COD, which are calculated assuming the complete oxidation of COD: 1 g COD = 1 g O_2. K = O_2/COD, K is oxygen excess coefficient. Fig. 2 shows the degradation rate of coking wastewater change with the oxygen excess coefficient.

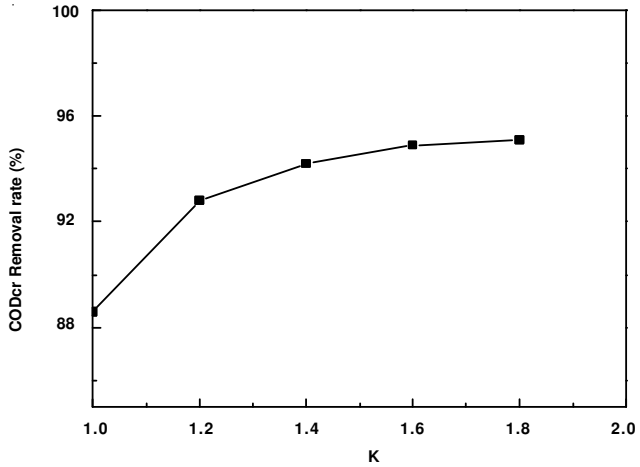

Fig. 2. Effect of H_2O_2 excess multiple on COD_{Cr} removal rate

As can be seen from Fig. 2, the degradation rate of coke plant wastewater has increased rapidly with the increase of the values of K. The degradation rate of coke plant wastewater almost unchanged when the values of K are more than 1.6. All the experiments were performed in condition of K = 1.6.

Effect of the reaction temperature: The effect of reaction temperature on COD_{Cr} removal rate was shown in Fig. 3, experiments conditions: reaction pressure 24 MPa, reaction time 1 min and k = 1.6.

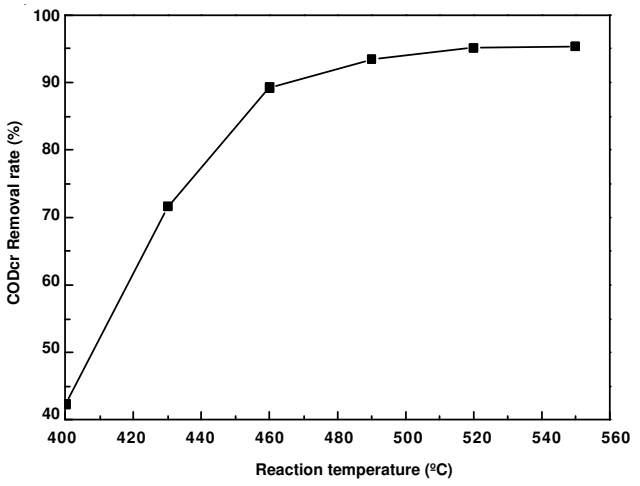

Fig. 3. Effect of reaction temperature on CODCr removal rate

It can be seen from Fig. 3 that the removal rate of COD_{Cr} is notably increased with the increase of reaction temperature range from 400-520 ºC. The result showed that temperature is a major factor in the degradation of coke plant wastewater. This is mainly because the reaction rate constant increases with the temperature increases, making the coke plant wastewater degradation rate increase rapidly. As the temperature continues to rise, although the removal rate of COD_{Cr} also improves, but the removal rate of COD_{Cr} is not very clear, because increasing temperature reduces the density of the reactant system and reactants (water, oxygen, organic matter) concentration, thereby reducing the speed of response. So the reaction temperature was chosen between 520-550 ºC.

Effect of reaction pressure: The effect of reaction pressure on COD_{Cr} removal rate was shown in Fig. 4, experiments conditions: reaction temperature 540 ºC, reaction time 1 min and k = 1.6.

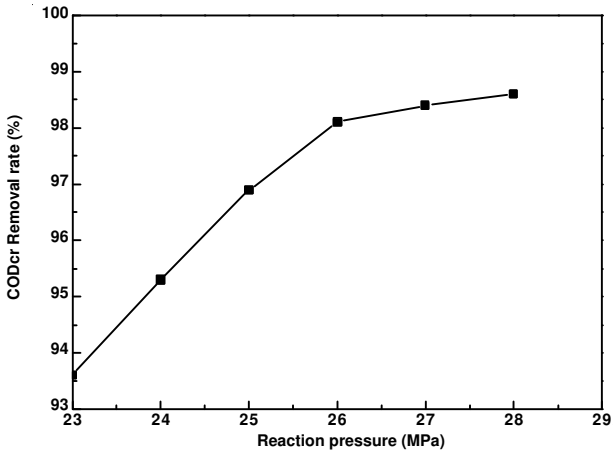

Fig. 4. Effect of reaction pressure on COD_{Cr} removal rate

It can be seen from Fig. 4 that removal rate of COD_{Cr} increased with reaction pressure increased, but with little effect, the reason may be: when temperature is constant, pressure increases result in increased water density, thereby increasing the reactant and oxidant concentration, the reaction rate turn to be faster. Meanwhile, the residence time of pollutant degradation in the reactor increases with the density of water increases, which is also conducive to the degradation of pollutants. Besides, the reaction temperature is 540 ºC, which is much higher than the critical temperature of water 374 ºC, in such a high temperature conditions, the reaction temperature was a main factors influencing of the properties of water and the increase of the pressure will greatly increase the burden on the equipment, therefore the reaction pressure of the actual production should not be too high and the proper reaction pressure was 27-28 MPa.

Effect of reaction time: The effect of reaction time on COD_{Cr} removal rate was shown in Fig.5, Experiments conditions: reaction temperature 540 ºC, reaction pressure 27MPa and k =1.6.

It can be seen from Fig. 5, with extending of the reaction time, the removal rate of COD_{Cr} have increased rapidly then leveled off. When the reaction time of 80 s, the removal rate of COD_{Cr} reaching 99 %, continue to extend the reaction time, removal rate of COD_{Cr} increase levels off, reaching 99.1 % in 2 min. When the residence time is long enough, the reaction rate decreases with the concentration of reactants decreases, the degradation rate of coke plant wastewater has becomes slow with increased of the residence time. Obviously, it is possible to obtain higher the removal rate of COD_{Cr} at the right temperature and pressure by extending the reaction time. The proper reaction time was greater than 2 min.

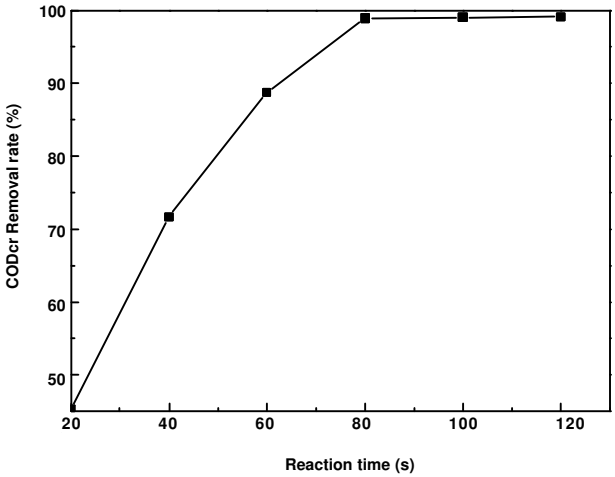

Fig. 5. Effect of reaction time on CODCr removal rate

Suitable conditions: Supercritical water oxidation is at high temperatures and high pressure, which means requirements of conditions on the equipment. So, by reducing the reaction pressure and temperature and extending residence time, the results of investigated conditions are in Table-1.

TABLE-1
EXPERIMENT CONDITIONS AND RESULTS

No.	Temperature (℃)	Pressure (MPa)	Reaction time (s)	K	COD_{Cr} (mg/L)
1	480	28	160	1.6	291.8
2	500	28	160	1.6	147.2
3	520	28	140	1.6	76.4
4	540	28	120	1.6	43.8
5	560	28	100	1.6	43.1

To ensure consistent treatment of coke plant wastewater abide by discharge standard GB8978-1996, the suitable conditions of the degradation of coke plant wastewater were ascertained. With the multiples of oxygen in excess of 1.6, the temperature 540 ℃, the pressure 28 MPa and the residence time over 2 min, the COD_{Cr} of coke plant wastewater was 43.8 mg/L.

Mineral deposition: Most of the minerals is very low solubility in supercritical water, when the sub-critical solution is rapidly heated to supercritical temperature, the reaction precipitation in a large number of deposition of mineral will cause the reactor block, owing to a significant reduction in the solubility of the mineral, which not only affects the normal operation of the reactor, but also is potentially dangerous. Coke plant wastewater mainly containing inorganic compounds are sulphur cyanide, sulfide, cyanide, *etc*., in order to avoid the impact of mineral deposition on test process, mineral-water separator was placed between liquid pre-heater and reactor, making part of the minerals were separated in the sub-critical state.

Conclusion

Coke plant wastewater was treated by using supercritical water oxidation process, the reaction temperature is the main factors which affect the removal of coke plant wastewater in excessive amount of hydrogen peroxide. The suitable conditions of supercritical water oxidation were: reaction temperature 520-550 ℃, reaction pressure 27-28 MPa, reaction time greater than the 2 min. In this condition, the removal rate of COD_{Cr} of coke plant wastewater is up to 99 %.

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