

Wet Air Oxidation and Catalytic Wet Air Oxidation for Refinery Spent Caustics Degradation

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Summary: The work focuses on evaluating wet air oxidation and catalytic wet air oxidation technique to degrade refinery spent caustics (original COD is 250,781 mg/L) in a milder operation conditions (150-200°C, 0.2-2.5MPa). The results show that: in non-catalyst WAO, the highest COD degradation conversion could reach about 75% when 200°C, 2MPa oxygen and 300rpm were used. At every temperature, the reaction procedures follow pseudo-first order equations and the activation energy is 45.5 kJ/mol. The reactivity of three main contaminants in wastewater is on the order of sulphide > petroleum > volatile phenol. The COD degradation conversion could improve to about 95% when composite catalyst MnO_x-CeO_x/γ-Al₂O₃ ($W_{Mn}/W_{\gamma-Al_2O_3}=0.5$ and $W_{Ce}/W_{MnOx/\gamma-Al_2O_3}=0.4$) was used. The pseudo-first order equations also could be applied for catalyst system and its activation energy decreases to 27.2 kJ/mol. The catalyst could improve the degradation efficiency of petroleum and volatile phenol. Their conversions could increase to 85% and 74% respectively after catalyst used.

Introduction

Petroleum industry occupies an important position in Chinese industrial structure. Nowadays, in China, about 70% industry products and 20% energy depend on petroleum industry. Meantime, petroleum industry brings China lots of environment problems involving water, air and solid pollutes. Currently, traditional sodium hydroxide wash-electricity technology is still used by most Chinese petroleum refining companies. The technology uses caustic (mainly NaOH solutions) to remove H₂S and organic sulfur compounds from hydrocarbon streams under high voltage electricity environment. The caustic could be recycled until the alkali solution loses its refinery ability. After expire, the caustic will be discharged and become wastewater called refinery spent caustics.

To be a high organic concentration, toxic and refractory effluent, refinery spent caustics contains sulphide, volatile phenols, petroleum and some other organic pollutants. If the effluent is discharged without any treatment, these various toxic components could directly contaminate water and soil environment. Amitava Bandyopadhyay has assessed a refinery wastewater discharge accident in Indian and advised that huge sum funds have to be cost to remediate the environment [1]. On the other hand, the toxic escaping gas (mainly the H₂S) from refinery spent caustics seriously threatens the industry staffs' health. Considering its high risk, refinery spent caustics has been classified by Chinese

government to National List of Dangerous Waste (No. HW-35) [2].

During the past decade, many researchers have been working on treating this dangerous effluent through many special biological methods. Marco de Graaff develops a continuously fed system to treat refinery spent caustics under halo-alkaline conditions [3]. Jan Sipma suggested that refinery spent caustics could be degraded by biological oxidation processes [4]. However, because biological method needs a rigor operational condition and its fragile resistance to impact load, a simpler and more efficient method must be improved.

Wet air oxidation (WAO) was suggested to be an effective technique for highly toxic and organic wastewater treatment in 1950s [5]. The technique applies O₂/air to oxide organic components in wastewater under an elevated temperature (150°C-400°C) and pressure (2MPa-5MPa). The high temperature improves the solubility and oxidation force of O₂ and the reaction environment is maintained in liquid phase because of elevated pressure. With the help of water for heat transformation, most organic compounds in wastewater are finally degraded to CO₂ or other small molecular innocuous products. Moreover, the air pollution could be effective controlled since most pollutants are limited in aqueous phase and the reaction generally occurred in a closed environment. Many researchers point out that WAO is ideally

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suitable for wastewaters which are too dilute to incinerate and too toxic or concentrated for biological treatment and it would be suitable for wastewaters with COD loads from 100000 to 1000000 mg/L. As a result, wet air oxidation should be applied for refinery spent caustics whose COD concentration usually ranges from 100000 to 300000 mg/L [6]. Ellis Tania proposed that WAO offers an attractive pre-treatment option which allows effective on-site treatment [7]. Carlos successfully uses WAO method (260°C and 8.8MPa) to treat refinery spent caustics in Brazil [8]. However, WAO has not got extensive usage so far because many engineers are afraid of its expensive operating cost associated with elevated temperature and pressures. Fortunately, with the development of related researches, the cost would be reduced because suitable catalysts are improved. I.Zermenõ-Montante suggested that it is possible to operate at considerable lower temperatures and pressures for sulfide oxidation to sulfates in spent caustics with a suitable catalyst for catalytic wet air oxidation (CWAO) [9]. The paper focuses on applying wet air oxidation technique to degrade refinery spent caustics in a milder operation conditions (150-200°C, 0.2-2.5MPa). An effective catalyst is successfully synthesized to improve the oxidation efficiency of refinery spent caustics. The results may give us an efficient way to refinery spent caustics treatment and also provide a basic understanding of its reaction mechanism.

Results and discussions

Wet air oxidation

As we know, for WAO equipment, it is a typical gas-liquid two-phase system, in which the oxygen transfers from the gas phase to the liquid phase and then the oxidation reaction courses in the liquid medium. Thus, oxygen transfer is one of important factors that must be considered for our WAO system. Before we carry out other experiments, the diffusional resistance of oxygen transfers has to be eliminated. To demonstrate the absence of external oxygen transfers limitations in our WAO system, the experiments are run at different oxygen partial pressures and stirring speed. From Fig. 1a, it could be seen that the effect of oxygen partial pressures on COD degradation conversion is positive but increasing the oxygen partial pressures above 2.0MPa did not change the COD degradation conversion significantly any longer. Fig. 1b gives us similar results that after 300rpm, COD degradation conversion reach a plateau. The results imply that at this specified conditions (2.0MPa and 300rpm), the oxygen transfer is no more limiting to the reaction

and external diffusional resistance could be eliminated. Under the same operating conditions, a true kinetically controlled reaction regime could be obtained.

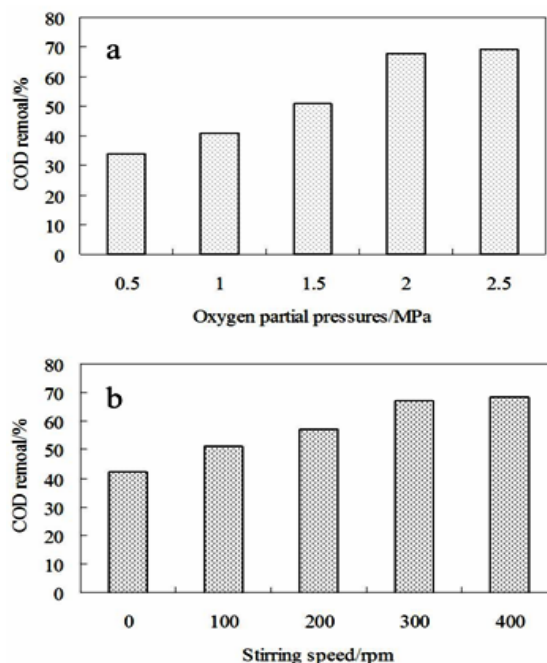


Fig. 1: Effect of oxygen partial pressures and stirring speed on COD decreases.

Fig. 2a shows how COD decreases as the function of reaction time at a series of reaction temperatures (150–200°C). The experiments are conducted at 2MPa oxygen partial pressure and 300rpm stirring speed. The highest COD degradation conversion could be gained at 200°C and the value is about 75%. Elevated temperature has been proved to be one of important factors that affect the oxidation rate of WAO. From Fig. 2a, it could be seen that the COD degradation conversion significantly increases with the temperature. For example, after 3h reaction, the final COD degradation conversion is about 75% under 200°C, while the value only reach about 30% under 150°C. On the other hand, Fig.2a also tells us that the positive effect of temperature to COD degradation conversion is limited and cannot be unrestrained improved. From 150 to 160°C, the final COD degradation conversion increases from 31% to 42% and the apparent rate is about 9% per 10°C. Nevertheless, from 190 to 200°C, the apparent rate of final COD degradation conversion decreases to about 2.4% per 10°C (from 73.2% to 75.6%). As we know, the temperature dependence of reaction could be accurately gained from Arrhenius equation as below:

$$K = Ae^{-Ea/RT} \quad (1)$$

$$\ln K = \ln A - \frac{Ea}{R} \cdot \frac{1}{T} \quad (2)$$

where K is the rate constant, T is absolute temperature of reaction, Ea is activation energy of reaction, A is Pre-exponential factor and R is gas constant (8.314 J/mole. K).

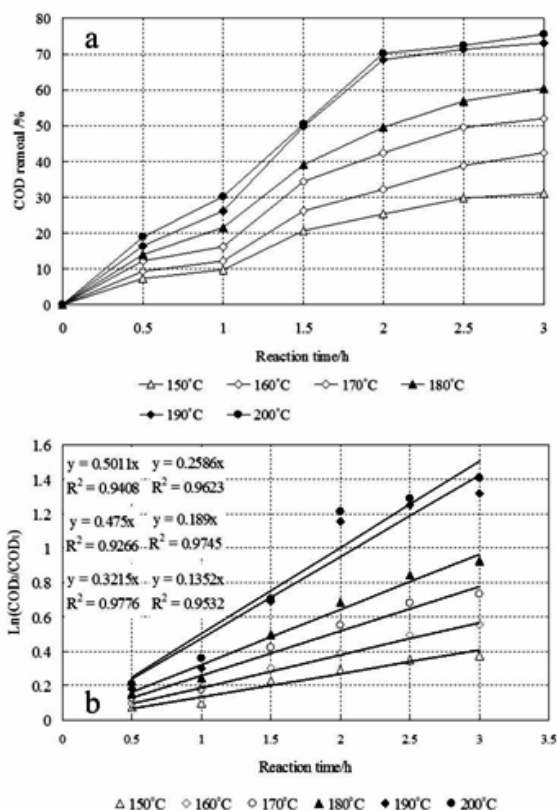


Fig. 2: Effect of reaction temperature on COD decrease and pseudo-first order plot of COD decrease on non-catalyst wet air oxidation

Before use this equation, the reaction rate constant at different temperature must be calculated by kinetics plot. Because refinery spent caustics is a high concentration effluent which contains sulphide concentration, volatile phenols and petroleum, the true kinetics model should be very complicated and difficult to study. On the other hand, from the environmental view, the more important item is final COD value but not the concentration of any reactant or intermediate. So the kinetics analysis is presented in term of COD degradation conversion and not with respect to individual components [10]. In our paper, the pseudo-first order equation as below is used:

$$-\frac{d(COD)}{dt} = K(COD) \quad (3)$$

$$\ln \frac{COD_0}{COD_t} = Kt \quad (4)$$

where t is reaction time (hour).

Fig. 2b demonstrates the results of kinetics analysis, it could be seen that the pseudo-first order equation is successfully applied to our WAO system and the rate constants are found as 0.5011, 0.475, 0.321, 0.259, 0.189, 0.135 hour⁻¹ at temperature of 150, 160, 170, 180, 190, 200°C, respectively. From this analysis, with the help of Arrhenius equation plot, the activation energy is got as 45.5 kJ/mol and the kinetics equation of reaction could be derived as follow:

$$-\frac{d(COD)}{dt} = (5.75 \times 10^4) \exp\left(\frac{-45500}{T}\right)(COD) \quad (5)$$

Fig. 3 reports the oxidation behavior of different composition in the wastewater (sulphide, volatile phenols and petroleum). The reactivity of three main composition is on the order of sulphide > petroleum > volatile phenols. The sulphide could be nearly 100% oxidized under every temperature from 150°C to 200°C, which could be considered to be an easily degradable contaminant for WAO. The results are consistent with I. Zermeño-Montante, who suggested that sulphide could be completed oxidation under mild temperatures [9]. To be a typical refractory organics, the oxidation conversion of volatile phenol is only about 13% under 150°C and 42% under 200°C in our experiments. The substituted phenol oxidation process could be divided into three steps: an induction phase where phenol concentration varies a little, a phase of rapid degradation and a final phase much slower when most of phenol is oxidized to finally phase, the molecules produced during the fast phase compete with the remaining phenol to react with the hydroxyl radicals and dissolved oxygen [11]. Because of this degradation mechanism, the volatile phenol oxidation conversion could not reach an accepted value unless temperatures higher than 200°C or a suitable catalyst is used. For petroleum, the oxidation conversion is about 66% under 200°C. As our opinions, the petroleum and volatile phenol should be the reason which restricts the increasing of COD degradation conversion. Generally, various intermediates (including acetic acid, formic acid, oxalic acid and some other short-chain organic acids) would form during the degradation process. The existence of these short-chain organic acids (could be calculated in COD results) and considerable un-oxidized initial organic compounds lead to the COD degradation conversion be doubtlessly limited in a relatively lower level.

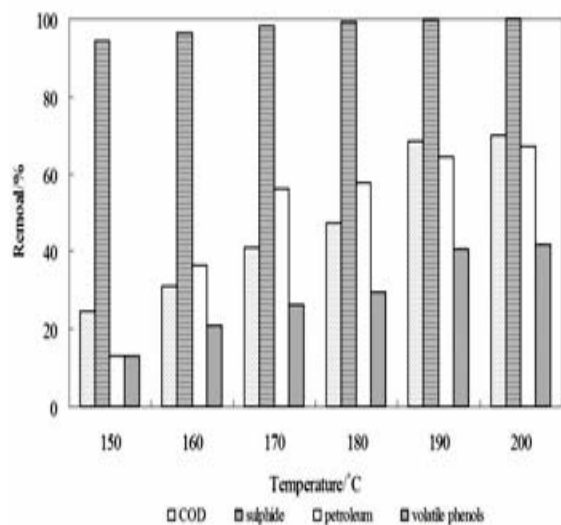


Fig. 3: Effect of reaction temperature on sulphide, volatile phenols and petroleum decrease

Catalytic Wet Air Oxidation

As results in Fig. 2a, the highest COD degradation conversion of non-catalytic WAO is about 75%. So, for refinery spent caustics whose original COD concentration reaches about 250,781 mg/L, the lowest residual COD concentration after non-catalytic WAO treatment is still at least 75,000mg/L. To improve the COD degradation conversion, catalytic wet air oxidation experiments have to be conducted. According to references, the catalysts applied for CWAO could be divided into two main types: the noble metal catalysts and common metal oxide catalysts. The noble metal catalysts include Ru, Rh, Rd, and Pt. γ - Al_2O_3 , TiO_2 , CeO_2 , ZrO_2 and carbon materials are usually used as their carriers. On the other hand, the main common metal oxide catalysts include CuO , CeO_2 , Fe_2O_3 , MnO_2 and their complexes [12-17]. Since the higher cost of noble metal catalysts, common metal oxide catalysts have attracted more attentions as alternatives for CWAO. Based on references and present research results, we choose catalysts are self-made MnO_x - CeO_x/γ - Al_2O_3 catalysts. Fig. 4 shows XRD patterns of catalysts with different $W_{\text{Ce}}/W_{\text{MnO}_x/\gamma\text{-Al}_2\text{O}_3}$ ratio. As Fig. 4, the strongest peaks in four patterns belong to γ - Al_2O_3 (2θ at 67.3, 45.8 and 37.3°). The peaks of CeO_2 (2θ at 28.6°) appear in two patterns (No.3 and 4), which should be resulted from higher CeO_x ratio. Different from γ - Al_2O_3 and CeO_2 , the peaks of Mn_3O_4 (2θ at 36.2 and 31.5°) were very hard to be observed and these implied that the MnO_x exist as an amorphous phase in all catalysts.

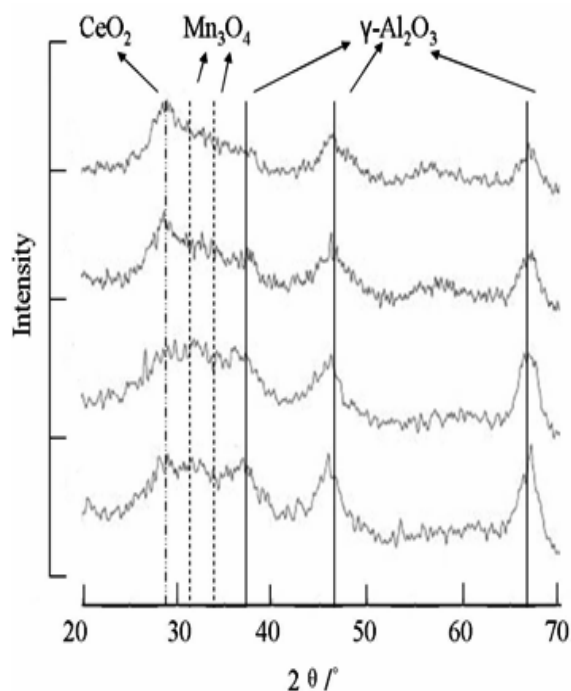


Fig. 4: XRD patterns of catalysts (The $W_{\text{Mn}}/W_{\gamma\text{-Al}_2\text{O}_3}$ ratio of every catalysts is 0.5 and $W_{\text{Ce}}/W_{\text{MnO}_x/\gamma\text{-Al}_2\text{O}_3}$ ratio ranges from 0.1% to 0.4%).

The COD degradation conversion results obtained from these catalysts system is given by Fig. 5 (Reaction time is 2h). As Fig. 5, compared with original non-catalytic system and other three catalyst systems, considerable increase of COD degradation conversion could be found in No. 4 catalyst systems. For example, after 2h reaction under 200°C, the COD degradation conversion of original non-catalytic system is only about 75%. In No. 4 catalysts system, the COD degradation conversion increases to about 95%. Similar results could be gained from other reaction temperatures. Temperature dependence study (temperature from 150 to 200°C) and kinetics plot (pseudo-first order equation) of No. 4 catalysts system are analyzed in similar manner as discussed in the case of WAO system (Fig. 6). The rate constants increased to 0.6115, 0.5305, 0.4521, 0.3816, 0.3636, 0.2535 hour^{-1} at temperature of 150, 160, 170, 180, 190, 200°C, respectively and the activation energies decreased to 27.2kJ/mol. The kinetics equation was changed as follow:

$$-\frac{d(\text{COD})}{dt} = 623 \exp\left(\frac{-27202}{T}\right)(\text{COD}) \quad (6)$$

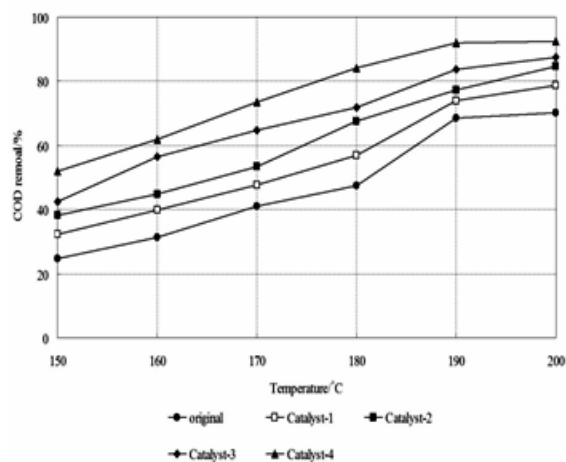


Fig. 5: Effect of catalysts on COD decreases.

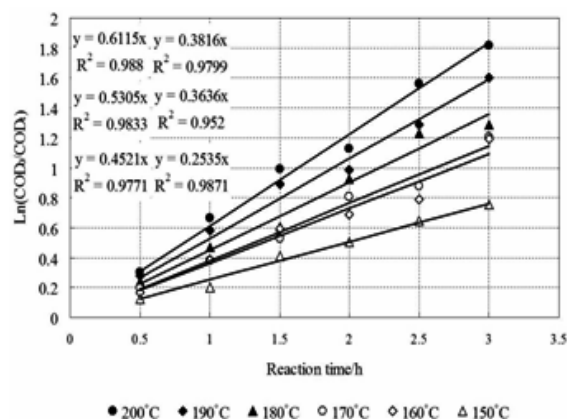


Fig. 6: pseudo-first order plot of COD decrease on catalyst wet air oxidation (No.4 catalyst system).

Fig. 7 compares the oxidation behavior of three main compositions (sulphide, volatile phenols and petroleum) in non-catalytic and No.4 catalytic WAO systems. The reaction temperature is 200°C and oxygen partial pressure is 2MPa. For sulphide, since nearly a complete transformation is obtained in non-catalytic wet air oxidation, adding $\text{MnO}_x\text{-CeO}_x/\gamma\text{-Al}_2\text{O}_3$ give little influence on the final conversion of sulphide but evident improvement of the depletion profiles are observed. In non-catalytic WAO, the sulphide conversion can not reach about 100% until the reaction temperature prolong to 1.5h. In contrast, $\text{MnO}_x\text{-CeO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst improves the oxidation efficiency and about 89% sulphide has been oxidized after only 0.5h. Chen suggested that Mn-Ce-O composite catalytic has significant effect on phenol degradation [18]. The results of Arena showed that improved MnCeOx catalysts could be

used for phenol oxidation in actual wastewater streams [19]. In our system, $\text{MnO}_x\text{-CeO}_x/\gamma\text{-Al}_2\text{O}_3$ shows significant catalytic ability on both volatile phenols and petroleum. The final conversion and apparent degradation rate of petroleum in $\text{MnO}_x\text{-CeO}_x/\gamma\text{-Al}_2\text{O}_3$ catalytic system are about 85% and 28.3% per hour, which are 21% higher than non-catalytic WAO system. Moreover, the adding of $\text{MnO}_x\text{-CeO}_x/\gamma\text{-Al}_2\text{O}_3$ brings a 59.6% increase for the final conversion and apparent degradation rate of volatile phenols (from 46.4% to 74.1% and 15.5% per hour to 24.7% per hour).

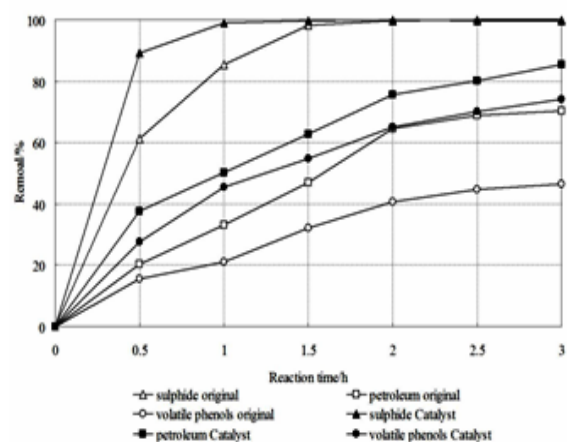


Fig. 7: Effect of catalyst (No.4) on oxidation behavior of different composition in the wastewater.

Experimental

Effluent

The refinery spent caustics studied in this paper was taken from China Petrochemical Corporation. The COD concentration was 250,781 mg/L, sulphide concentration was 13200 mg/L, volatile phenols was 36800mg/L, petroleum was 3470 mg/L. No pre-treatment was carried out before wet/catalytic air oxidation equipment.

WAO Procedure

The milder WAO procedures were conducted in a batch mode using a steel apparatus. The apparatus were bought from Dalian Automatic instrument factory (China). The model number was GCF2a-2. The apparatus contained a reaction vessel (1L), inlet and outlet gas/liquid sampling lines, a mechanical stirrer, an axial thermocouple and some other attachments, respectively. The maximal working temperature and pressure were 350°C and 40MPa. The fluctuation of working temperature was $\pm 1^\circ\text{C}$.

In a typical run, 300 ml effluent was poured into reaction vessel, and then the apparatus was mechanical seal. After this, the heating device started working and pure oxygen started being pumped into the reaction vessel. The apparatus could reach working status in about half an hour. At the end of reaction, the heating device and oxygen pumping were stopped and the whole apparatus was cooled by circulating cooling water to room temperature. Finally, the effluent was taken out from the vessel and put into a polyethylene bottle.

CWAO Procedure

The catalyst used in CWAO is synthesized by a fractional impregnation method. Firstly, 100g γ - Al_2O_3 power (BET surface area 170 m^2/g , pore diameter 10 nm, Jiangsu chemical company) is put into $\text{Mn}(\text{NO}_3)_4$ solution. The $W_{\text{Mn}}/W_{\gamma\text{-Al}_2\text{O}_3}$ is fixed at 0.5% and the impregnation process is conducted under room temperature by a stirring device for 24h. After this, the mixture is dried under 105°C for another 24h and then incandescenced under 600°C in a muffle furnace for 6h. Secondly, 100g made $\text{MnO}_x/\gamma\text{-Al}_2\text{O}_3$ solid is put into $\text{Ce}(\text{NO}_3)_3$ solution. The $W_{\text{Ce}}/W_{\text{MnO}_x/\gamma\text{-Al}_2\text{O}_3}$ ranges from 0.1% to 0.4%. The impregnation process is same as above and final product is $\text{MnO}_x\text{-CeO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst. Table-1 shows mass ratio of reactants for making catalysts. The milder CWAO procedures were the same as first stage but 0.3g $\text{MnO}_x\text{-CeO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst was put into the system.

Table-1: Mass ratio of reactants for catalysts.

No.	$W_{\text{Mn}}/W_{\gamma\text{-Al}_2\text{O}_3}$	$W_{\text{Ce}}/W_{\text{MnO}_x/\gamma\text{-Al}_2\text{O}_3}$	Mass of $\gamma\text{-Al}_2\text{O}_3$ (g)	Mass of $\text{Mn}(\text{NO}_3)_4$ (g)	Mass of $\text{Ce}(\text{NO}_3)_3$ (g)
1	0.5	0.1	100	2.25	0.238
2	0.5	0.2	100	2.25	0.476
3	0.5	0.3	100	2.25	0.714
4	0.5	0.4	100	2.25	0.952

Analysis Method

The COD, sulphide, volatile phenols and petroleum analysis are according to Chinese standard methods for water quality examination made by Chinese Environmental Protection Department (GB 11914-89 for COD, GB/T 5195.4-2006 for sulphide, CJ/T 58-1999 for volatile phenols, GB/T16488-1996 for petroleum). Before test, some higher concentration sample is diluted to fit the test range of these methods.

Conclusion

The paper studies applying wet air oxidation and catalytic wet air oxidation technique to degrade

refinery spent caustics in a milder operation conditions (reaction temperature from 150°C to 200°C and oxygen partial pressures from 0.5MPa to 2.5MPa). The results demonstrated that the effluent (original COD concentration is 250,781 mg/L) could be degraded by wet air oxidation technique under the milder conditions and the degradation conversion could be improved after a suitable catalyst is ($\text{MnO}_x\text{-CeO}_x/\gamma\text{-Al}_2\text{O}_3$, $W_{\text{Mn}}/W_{\gamma\text{-Al}_2\text{O}_3}=0.5$ and $W_{\text{Ce}}/W_{\text{MnO}_x/\gamma\text{-Al}_2\text{O}_3}=0.4$) used. For non-catalyst wet air oxidation, COD degradation conversion could reach highest 75% when experiments are operated under 200°C and 2MPa for 3h. The reactivity of three main contaminants in wastewater is on the order of sulphide > petroleum > volatile phenol. The composite catalyst ($\text{MnO}_x\text{-CeO}_x/\gamma\text{-Al}_2\text{O}_3$, $W_{\text{Mn}}/W_{\gamma\text{-Al}_2\text{O}_3}=0.5$ and $W_{\text{Ce}}/W_{\text{MnO}_x/\gamma\text{-Al}_2\text{O}_3}=0.4$) has an effective catalytic activity, by which, the COD degradation conversion could increase to 95% under 200°C and 2MPa. The catalyst also show positive effect in the oxidation of petroleum and volatile phenol and their conversions could increase to 85% and 74% respectively after catalyst used. The pseudo-first order equations could be successfully applied for non-catalyst and catalyst wet air oxidation system and the activation energy is 45.5 and 27.2 kJ/mol , respectively.

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