



Study on the treatment of 2-*sec*-butyl-4,6-dinitrophenol (DNBP) wastewater by ClO₂ in the presence of aluminum oxide as catalyst

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ABSTRACT

The chlorine dioxide (ClO₂) oxidative degradation of 2-*sec*-butyl-4,6-dinitrophenol (DNBP) in aqueous solution was studied in detail using Al₂O₃ as a heterogeneous catalyst. The operating parameters such as the ClO₂ concentration, catalyst dosage, initial DNBP concentration, reaction time and pH were evaluated. Compared with the conventional ClO₂ oxidation process without the catalyst, the ClO₂ catalytic oxidation system could significantly enhance the degradation efficiency. Under the optimal condition (DNBP concentration 39 mg L⁻¹, ClO₂ concentration 0.355 g L⁻¹, reaction time 60 min, catalyst dosage 10.7 g L⁻¹ and pH 4.66), degradation efficiency approached 99.1%. The catalyst was used at least 8 cycles without any appreciable loss of activity. The kinetic studies revealed that the ClO₂ catalytic oxidation degradation of DNBP followed pseudo-first-order kinetics with respect to DNBP concentration. The ClO₂ catalytic oxidation process was found to be very effective in the decolorization and COD_{Cr} reduction of real wastewater from DNBP manufacturing. Thus, this study showed potential application of ClO₂ catalytic oxidation process in degradation of organic contaminants and industrial effluents.

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1. Introduction

Phenolic compounds are a group of persistent organic pollutants that pose serious risks to the environment and human health once discharged into natural water. Some of the most toxic compounds of this class are those nitro-substituted phenol compounds. 2-*sec*-butyl-4,6-dinitrophenol (DNBP) is a typical example of this class of toxic nitro-substituted phenol compounds. DNBP is widely used as polymerization inhibitor for vinyl aromatics in petrochemical industry and as herbicide in agriculture. It is introduced into surface water from its manufacturing and application processes. Because of its toxicity and poor biodegradability, DNBP wastewater must be specially treated before disposed off. There have been several different treatment techniques available for the removal or elimination nitrophenols from wastewater such as adsorption by activated carbon-cloth [1], photocatalytic oxidation [2], Fenton or Fenton-like reactions and photo-Fenton or photo-Fenton-like reactions [3–5], biodegradation treatment [6], etc. However, such technologies usually do not involve easy procedures or are not economical. ClO₂ oxidation was a very attractive and useful technique for treatment of different kinds of effluents [7–9].

Since 1940s when ClO₂ was firstly used in the United States for water treatment, current applications of ClO₂ in drinking

water treatment include disinfection [10], nitrification [11] and bromate control [12]. Moreover, the oxidation potential makes ClO₂ a technique to destroy pollutants in wastewater. ClO₂ is effective for removing iron, manganese [13] and cyanide [14]. And it has been found to be useful for treatment of dyehouse effluents [15]. However, the traditional ClO₂ oxidation process has not been largely implemented for DNBP wastewater treatment because it resists to conventional chemical oxidation due to the strong electron-withdrawing property of the two nitro groups on the benzene ring, resulting in the comparative low oxidative degradation efficiency, long reaction time and high economical costs. ClO₂ catalytic oxidation process is a well-established technique to decompose toxic and nonbiodegradable organic compounds in wastewater [16], which is able to oxidize organic pollutants into carbon dioxide or small molecules that can be eliminated easily by conventional wastewater treatment methods or biological process. A CuO_n-La₂O₃/γ-Al₂O₃ catalyst which was prepared by impregnation–deposition method was used in the ClO₂ oxidation process assisted by microwave. It could effectively degrade phenol and remazol golden yellow dye in wastewater in short reaction time and with low oxidant dosage, extensive pH range compared with no catalyst process [17,18]. However, the catalyst used in the ClO₂ catalytic oxidation process was not economical because of the adding of noble metal. Pure alumina as a heterogeneous catalyst for catalytic ozonation has been reported in the literature [19], but the application of alumina as catalyst for ClO₂ oxidation process in the treat-

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ment of wastewaters containing organic pollutants still remains unexplored.

In this paper, the performance of ClO_2 in the presence of aluminum oxide as catalyst for aqueous degradation of DNBP, which was chosen as a typical alkyl dinitro phenol organic pollutant, was investigated thoroughly and the reaction conditions in this system have been optimized. The main objective of our work is determining the optimal conditions of experimental parameters for the practical application of toxic organic wastewater by ClO_2 catalytic oxidation process.

2. Experimental

2.1. Materials

Chlorine dioxide was prepared via reacting potassium chlorate with hydrogen peroxide in sulphuric acid media [9]. The resulting gas was collected and dissolved in double distilled water. The stock ClO_2 solution was stored in dark at 4°C and was standardized before using. DNBP was used as an alkyl dinitro phenol pollutant and obtained from Retell Fine Chemical Co., Ltd. (Tianjin, China). The commercial aluminum oxide used as heterogeneous catalyst was purchased from Shanghai Wusi Chemical Reagent Co., Ltd., China. It was washed 3 times in deionized water, filtrated and then dried in an oven at 80°C for 10 h prior to further use. All other chemicals and reagents used in this study, including sulfuric acid, sodium hydroxide, etc. were AR grade from Tianjin Kermel Chemical Reagent Co. Ltd., China. All the reagents were used without any further purification. A stock solution of DNBP (39 mg L^{-1}) was prepared by dissolving DNBP in deionized water. Further solutions of different concentrations were made using the same stock solution.

2.2. Oxidative degradation of DNBP

Oxidative degradation reaction between ClO_2 and DNBP was carried out using 150 mL conical borosilicate glass sealed reactors in which 50 mL of synthetic wastewater containing 39 mg L^{-1} DNBP solution was placed. In an ordinary ClO_2 catalytic oxidation test, a known amount of catalyst was added into each conical borosilicate glass reactor containing DNBP solution under stirring. After stirring continuously for 60 min to ensure establishment of adsorption/desorption equilibrium of DNBP, certain amounts of the stock ClO_2 solution were introduced into the reactor with continuous stirring and it was treated as the starting point ($t=0$) of the reaction. For analysis, sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) was added to the sample immediately at selected intervals to dechlorinate ClO_2 residuals. The samples were then filtered and the filtrate was centrifuged at 6000 rpm for 5 min before analysis. All the experiments were carried out at room temperature ($25 \pm 1^\circ\text{C}$). Solution pH, ClO_2 concentration and catalyst loading were investigated for their effect on the oxidation performance in terms of the percent degradation efficiency ($\eta\%$), which can be calculated using the equation given below:

$$\eta(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C_0 and C are the concentration of DNBP at $t=0$ and t , respectively.

2.3. Analytical methods

The X-ray diffraction (XRD) pattern of the catalyst was recorded on a D/max-2400 diffractometer (Rigaku Industrial Corporation, Japan) using $\text{Cu K}\alpha$ radiation (40 kV, 30 mA) with a scan rate of $6.0^\circ 2\theta \text{ min}^{-1}$. The identification of compounds was done using the ICDD library. The microtextural characteristic of the catalyst was deter-

mined by nitrogen adsorption at 77 K (Micromeritics ASAP 2010 system, USA). The Brunauer–Emmett–Teller (BET) surface area [20] and pore volume of the catalyst was determined using the software available with the instrument. The pH drift method [21] was used to determine the pH at the point of zero charge (pH_{zpc}) of the catalyst surface using 50 mL of 0.1 M NaCl in a series of Erlenmeyer flasks whose pH were adjusted using 0.1 M NaOH and 0.1 M HCl in the range between 2 and 12. The initial pH of the solutions was determined and 0.15 g of the catalyst was added to each of the flasks and after completion of 48 h, the final pH of the solutions was measured. pH_{zpc} was noted at the pH in which the initial pH equals the final pH. The pH measurements were made using a Mettler–Toledo digital pH meter (model Delta 320-S).

The concentration of ClO_2 in the stabilized chlorine dioxide stock solution was measured by the iodometry method. The concentration of DNBP solution (C) during the oxidative degradation process was quantified by high performance liquid chromatography (HPLC) (Hewlett-Packard, HP series 1100) (CA, USA), comprising quaternary pumps, a UV detector and an auto sampler. In the HPLC analysis, a ZOBAX $5\ \mu\text{m}$ C18 ($4.6\text{ mm} \times 250\text{ mm}$) column was employed and a mobile phase of methanol/water (7:3, v/v) was used at a flow rate of 1.0 mL min^{-1} . An injection volume of $20\ \mu\text{L}$ was used and the concentration of DNBP was determined by the UV detector at 271 nm.

The chemical oxygen demand (COD_{Cr}) was determined by microwave digestion method described in the literature [22]. The conventional 5-day biochemical oxygen demand (BOD_5) determination was carried out following Standard Methods recommendations [23]. Acute toxicity of the real wastewater samples before and after treatment was analyzed the Luminescent bacteria test using a DXY-2 fast biological toxicity analyzer (Institute of Soil Science, Chinese Academy of Sciences) according to the method recommended by the manufacturer. The sample pH was adjusted to 7 with 1 M NaOH solution prior to toxicity test. The median effective concentration (EC_{50}) of the sample indicated the degree of toxicity of the sample.

3. Results and discussion

3.1. Characterization results

The point of zero charge (pH_{zpc}) of the catalyst is 7.75 determined by the pH drift method. The XRD pattern of the catalyst is shown in Fig. 1. As shown in Fig. 1, the XRD pattern of the catalyst used in the study contains the same characteristic peaks as that of

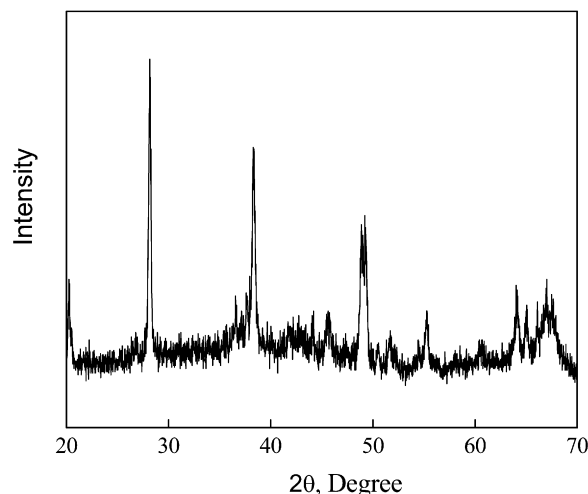


Fig. 1. XRD pattern of the Al_2O_3 catalyst.

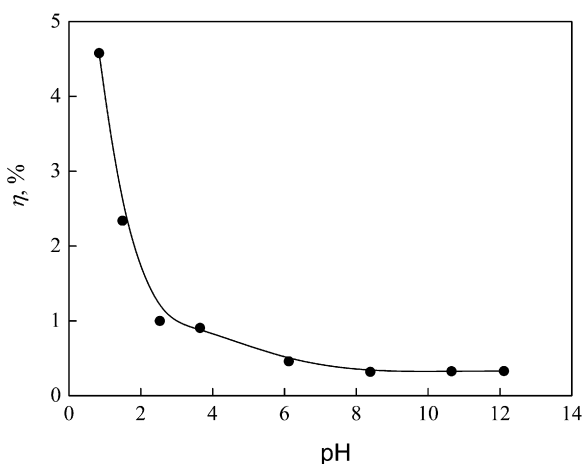


Fig. 2. Effect of pH on removal efficiency by adsorption.

α - Al_2O_3 [24]. The BET surface area of the catalyst was found to be $102.23 \text{ m}^2 \text{ g}^{-1}$. Corresponding pore volume of the catalyst was less than $0.40 \text{ cm}^3 \text{ g}^{-1}$ with a mean pore size of 14 nm.

3.2. Effect of pH

3.2.1. Effect of pH on adsorption

It is known that the first stage in heterogeneous catalytic systems is the adsorption of the target reactant to the surface of the catalyst. So the effect of pH on the adsorption of DNBP by the catalyst was investigated at different medium pH values ranged from 0.81 to 12.03 at present system (39 mg L^{-1} DNBP concentration, 10.7 g L^{-1} Al_2O_3 , 60 min contact time, 25°C). In all the experiments, pH was adjusted by adding appropriate amounts of H_2SO_4 or NaOH solutions. The results are shown in Fig. 2. It can be found that the removal efficiency decreased sharply with the increase of pH up to 6.0 and no obvious change was observed in the pH range 6.0–12.09. This might be explained by pH_{zpc} of the catalyst (7.75) and the pK_a of DNBP (4.62). At pH lower than pH_{zpc} , DNBP was mainly undissociated and the dispersion interactions predominated. However, for pH higher than pH_{zpc} , the uptake of DNBP was less and decreased sharply, because of electrostatic repulsions between the negative catalyst surface charge and the DNBP anions and between dinitrophenolate–dinitrophenolate anions in solution.

3.2.2. Effect of pH on degradation

The wastewater usually has a wide range of pH values. Furthermore, some wastewater treatment methods are also pH dependent. Thus, the initial pH is an important parameter influencing the performance of ClO_2 oxidation process. In order to examine the effect of pH values on the oxidative process, experiments were performed at different pH ranged from 0.81 to 12.03 with and without catalyst using the following experimental conditions: 39 mg L^{-1} DNBP concentration, 0.234 g L^{-1} ClO_2 , 10.7 g L^{-1} catalyst, 25°C and 60 min reaction time. The results are presented in Fig. 3. It can be seen that the existence of Al_2O_3 can effectively improve the DNBP removal of ClO_2 oxidation system. The degradation efficiency for DNBP increases quickly from initial pH 0.81 to 3.68. Beyond pH value of 6.14, the degradation efficiency starts to decrease, which indicates that the optimum pH value in catalytic system ranges from 3.68 to 6.14. Therefore, further experiments were performed at initial solution pH (4.66) without changing the pH.

The reaction between phenols and ClO_2 can be regarded as the single electron transfer process which has been confirmed by ab initio calculations [25]. It is generally accepted that one ClO_2 reacts with a phenoxide ion to give ClO_2^- and a phenoxy radical, which is

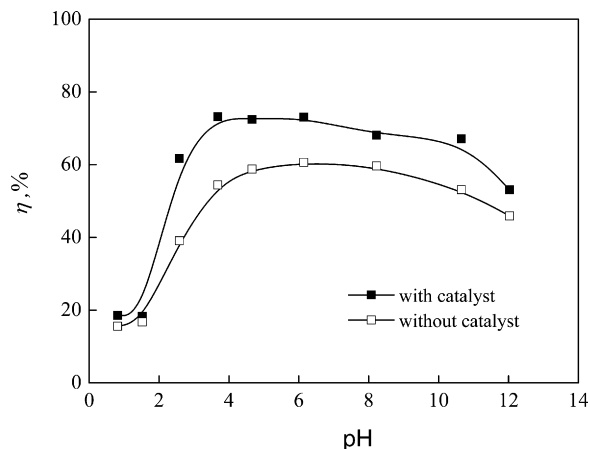


Fig. 3. Effect of the initial pH value on DNBP degradation efficiency.

the step that controls the overall reaction rate. Then, the phenoxy radical could react rapidly with a second ClO_2 . DNBP mainly exists in its molecular form at $\text{pH} < 3.68$, which is unfavorable to the reaction with ClO_2 according to the mechanism mentioned above. At alkaline conditions, ClO_2 reacts with OH^- to form chlorite (ClO_2^-) and chlorate (ClO_3^-) species [7], leaving less ClO_2 available for the reaction with DNBP. Furthermore, an increase in medium pH also results in the faster decomposition of ClO_2 .

3.3. Effect of ClO_2 concentration on degradation

The effect of ClO_2 concentration on the removal process was performed using following experimental conditions: 39 mg L^{-1} DNBP concentration, pH 4.66, 10.7 g L^{-1} catalyst, 25°C and 60 min reaction time. The results are presented in Fig. 4, which reveals that the degradation efficiency increased with an increase in ClO_2 concentration, up to 0.355 g L^{-1} , and thereafter, it increased slightly. The result indicates that the optimum ClO_2 concentration for degradation of DNBP is 0.355 g L^{-1} while the molar ratio of ClO_2/DNBP is 31.7. The results clearly show that, with catalyst, the removal percentage of DNBP is much higher than that without catalyst, which indicates that Al_2O_3 could obviously improve the DNBP degradation efficiency.

The effect of ClO_2 concentration on the reaction rate was investigated over the concentration range of 0.036 – 0.213 g L^{-1} (0.526 – $3.156 \text{ mmol L}^{-1}$) with a fixed DNBP concentration (39 mg L^{-1}) and catalyst loading (10.7 g L^{-1}). The concentration of DNBP was plotted as the function of reaction time t and

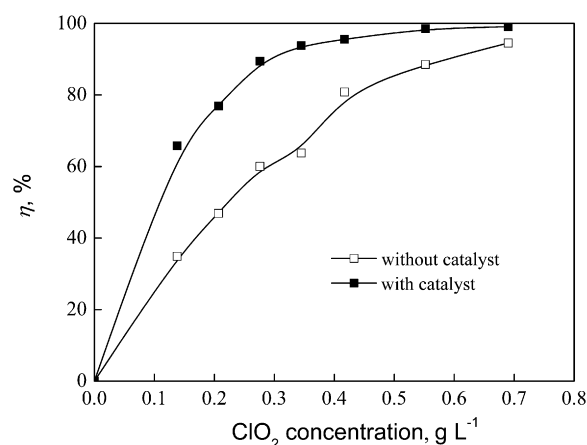


Fig. 4. Effect of initial concentration of ClO_2 on DNBP degradation efficiency.

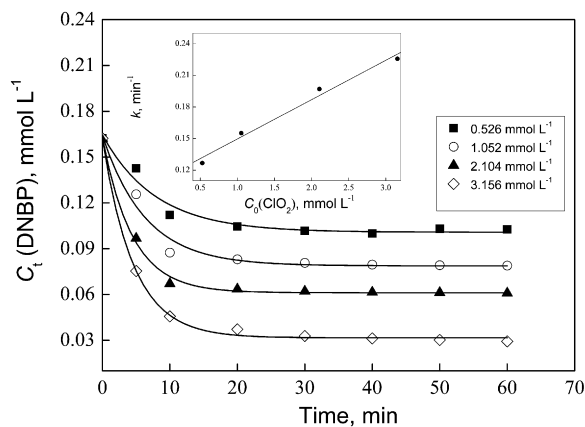


Fig. 5. Changes of DNBP concentration during the ClO_2 catalytic oxidation process with different initial ClO_2 concentrations (inset is the relationship between the obtained rate constant k and initial concentration of ClO_2).

the experimental results are shown in Fig. 5. It can be seen that the plots decay exponentially, which suggests the oxidative degradation experiments follow the pseudo-first-order kinetics with respect to the concentration of DNBP [26]:

$$C = A \exp(-kt) \quad (2)$$

where C is the concentration of DNBP, k is the rate constant, t is the reaction time and A is a constant. This equation predicts a linear plot between values of $\ln C$ and t . The rate constant k can be calculated using the slope of the straight line. The calculated kinetic constant k over the ClO_2 concentration range of $0.526\text{--}3.156 \text{ mmol L}^{-1}$ are in the range $0.1267\text{--}0.2257 \text{ min}^{-1}$. Fig. 5 inset indicates that there exists a linear relationship between the obtained rate constant k and the initial concentration of ClO_2 in the concentration range studied. The obtained dependence can be described by the following equation:

$$k = 0.112 + 0.037C_0(\text{ClO}_2)(R^2 = 0.991)$$

3.4. Effect of catalyst dosage on degradation

The effect of catalyst dosage on DNBP removal was performed using following experimental conditions: 39 mg L^{-1} DNBP concentration, 0.355 g L^{-1} ClO_2 concentration, pH 4.66, 25°C and 60 min reaction time. Fig. 6 illustrates that the degradation efficiency

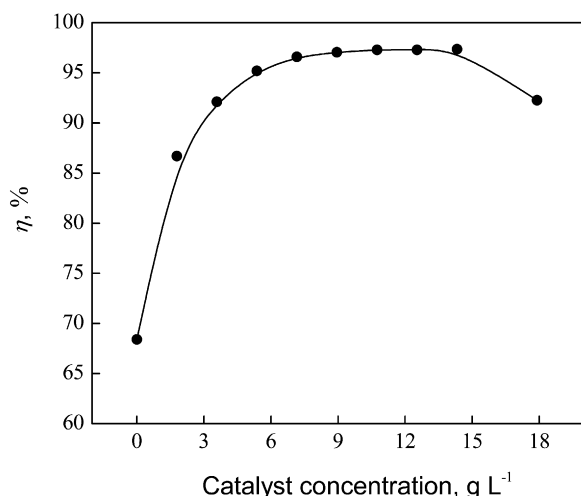


Fig. 6. Effect of catalyst dosage on DNBP degradation efficiency.

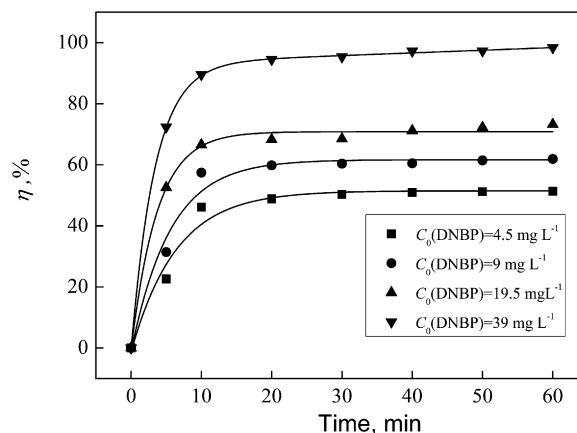


Fig. 7. Effect of various initial DNBP concentrations on the ClO_2 catalytic oxidation process.

increased with catalyst dosage, up to 10.7 g L^{-1} , and, thereafter, it leveled off. Within the range of catalyst dosage from 0 to 10.7 g L^{-1} , the observed enhancement in degradation may be due to adequate active catalytic sites available for the degradation reaction. This indicates that an optimized catalyst concentration (10.7 g L^{-1}) is necessary for enhancing the degradation efficiency.

3.5. Effect of initial DNBP concentration on degradation

The effect of initial DNBP concentration on the degradation efficiency was investigated by varying the initial concentration of DNBP from 4.5 to 39 mg L^{-1} ($0.018\text{--}0.1623 \text{ mmol L}^{-1}$). The degradation efficiency was decreased by increasing initials concentrations as expecting (Fig. 7). This could be attributed to the fact that ClO_2/DNBP molar ratio decreases as the concentration of DNBP increases.

The oxidative degradation experiments containing Al_2O_3 catalyst follow the pseudo-first-order kinetics with respect to the concentration of DNBP (Fig. 8). The calculated rate constant k over the DNBP concentration range of $0.018\text{--}0.1632 \text{ mmol L}^{-1}$ are in the range $0.2723\text{--}0.1568 \text{ min}^{-1}$. Fig. 8 inset shows the obtained rate constant k has a linear relationship with the initial concentration of DNBP. The obtained dependence can be described by the following equation:

$$k = 0.28377 - 0.80378C_0(\text{DNBP})(R^2 = 0.993)$$

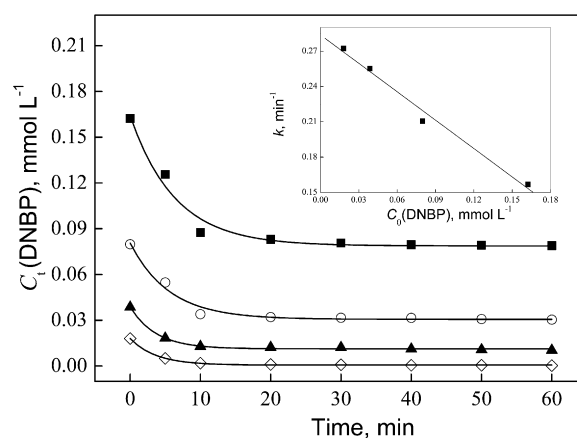


Fig. 8. The influence of various initial DNBP concentrations on the ClO_2 catalytic oxidation process (inset is the relationship between the obtained rate constant k and initial concentration of DNBP).

3.6. Effect of reaction time on degradation

The effect of reaction time on the ClO_2 oxidation process was performed using following experimental conditions: 39 mg L^{-1} DNBP concentration, 0.355 g L^{-1} ClO_2 , pH 4.66, 25°C and 10.7 g L^{-1} catalyst. In the ClO_2 oxidation process with Al_2O_3 , the degradation rate increased sharply and the removal of DNBP reached more than 90% after 5 min. In the ClO_2 catalytic oxidation process, the degradation efficiency was almost 100% after 20 min while that of ClO_2 oxidation process without catalyst was only 70% for the same reaction time. Al_2O_3 as catalyst could absorb DNBP, but the ability was very weak, the absorption of DNBP was only 5%. Therefore, it is indicated that the catalyst could not only improve the removal percentage of DNBP but also shorten the reaction time, suggesting this ClO_2 catalytic oxidation process had advantages for the engineering application.

3.7. Repetitive use of the catalyst

The reuse tests were performed in order to evaluate the catalytic activity of Al_2O_3 during successive experiments and thus to observe the possibility of catalyst reuse. The catalyst was used in eight consecutive experiments by using fresh DNBP solutions at optimum conditions (39 mg L^{-1} DNBP concentration, 0.355 g L^{-1} ClO_2 , pH 4.66, 25°C , 10.7 g L^{-1} catalyst and 60 min reaction time). Between each experiment, the catalyst was removed by filtration and then washed with deionized water for several times and dried at 50°C for overnight. Noticeably, the removal percentage of DNBP decreased only approximately 4%, from 99.1% to 95.2% after eight cycles. Furthermore, the activity of the catalyst after eight cycles could be recovered by calcining it in a muffle furnace at 300°C for 2 h. This indicates that the catalytic activity of Al_2O_3 catalyst has repeatability. The slight reduction in the degradation efficiency among the cycles may be explained by the formation of by-products and their accumulation on the active surface sites of the catalyst.

3.8. Degradation mechanism

To the best of our knowledge, there have been no reports on the catalytic oxidation of dinitrophenols using ClO_2 and Al_2O_3 . The mechanism of the ClO_2 catalytic degradation was not very clear. For the efficiency of the ClO_2 catalytic processes, the strong oxidizing ability of ClO_2 plays major role within the series of reactions taking place throughout the oxidative degradation processes. With strong oxidizing properties, ClO_2 itself can oxidize a range of organic pollutants with resulting production of oxidation by-products. It has been also proposed that the catalyst surface oxygenous group can initiate the ClO_2 to be changed into free radicals, such as $\cdot\text{OH}$, and subsequent oxidation of adsorbed DNBP via free radical pathways [18,27]. To verify the above mentioned theory, 0.5 mL of tertiary butyl alcohol which served as $\cdot\text{OH}$ -scavenger [28] was added to ClO_2 catalytic oxidation system under the optimal experimental conditions (39 mg L^{-1} DNBP concentration, pH 4.66, 10.7 g L^{-1} and 0.355 g L^{-1} of Al_2O_3 catalyst and ClO_2 , respectively). It was found that the degradation appeared to decrease and 90.2% degradation efficiency was observed with the addition of tertiary butyl alcohol. It was indicated that the quantity of $\cdot\text{OH}$ generated in the ClO_2 oxidation system increased by the addition of Al_2O_3 as a catalyst. Perhaps, in the above ClO_2 catalytic oxidation process, $\cdot\text{OH}$ could be generated by a free radical chain auto-oxidation process [18].

GC/MS–MS analyses were used to detect the intermediate products of DNBP degradation. The samples taken at different time intervals during degradation reaction were filtered and evaporated on a rotatory evaporator at 40°C . The residue was dissolved in 10 mL of dichloromethane and sonicated for 10 min. Then, the solution was reduced to about 1 mL by evaporation under N_2 and the

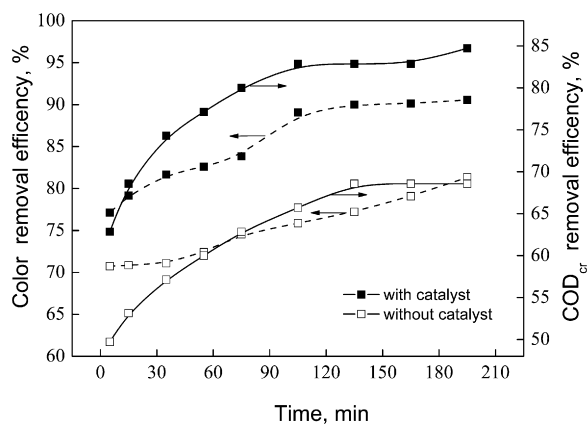


Fig. 9. Color and COD removal efficiency for real wastewater from DNBP manufacturing in ClO_2 oxidation process with and without catalyst.

resulting samples were injected into the GC–MS system (Agilent 6890 GC and 5793 MS) for analysis. From the GC/MS–MS analyses described above, the intermediate compounds during ClO_2 catalytic oxidative degradation of DNBP were identified as 3,5-dinitrocatechol, 3,5-dinitro-*o*-benzoquinone, maleic acid, oxalic acid. These intermediate compounds may be subjected to further degradation and eventually mineralized to CO_2 and H_2O .

3.9. Treatment of wastewater from DNBP manufacturing

From a practical point of view, there is a need to investigate the application of ClO_2 catalytic oxidation process for the degradation of nitrophenols from real wastewater. We conducted a study to determine the potential use of ClO_2 catalytic oxidation process for decolorization and chemical oxygen demand (COD_{Cr}) reduction of wastewater from DNBP manufacturing. The original wastewater with orange red color for the experiments was provided by Tairui, Inc. (Dalian, China). Results from an analyses of the wastewater are given as follows: pH 3.11, COD_{Cr} 5200 mg L^{-1} , colority 2000 times, turbidity value $>100 \text{ NTU}$, total phenols $>500 \text{ mg L}^{-1}$. Experiments were carried out using the real wastewater (diluted 1:20) with 20 g L^{-1} catalyst, 1.20 g L^{-1} ClO_2 and 200 min reaction time to investigate the removal of color and reduction in COD_{Cr} . Fig. 9 presents the reduction in COD_{Cr} and color of the wastewater with and without the catalyst. The removal of COD_{Cr} and decrease in color for the wastewater were 84.8% and 90.5% in the ClO_2 oxidation process with catalyst, respectively, while that of ClO_2 oxidation process without catalyst were 68.5% and 79.3%, respectively. The effect of catalyst in process is so clear that COD_{Cr} and color reduction are increased by more than 16.3% and 11.2% compared with no catalyst. Therefore, in the ClO_2 catalytic oxidation process, ClO_2 and catalyst work together to improve the pollutants removal efficiency. The BOD_5/COD value increased from 0.052 in the initial stage to 0.528 after 200 min treatment, which confirms the good biodegradability of the wastewater. The 15 min-EC50 values of the wastewater at time 0 and after 200 min treatment were 0.352% and 86.356%, respectively, indicating that the toxicity of reaction intermediates produced from ClO_2 catalytic oxidation process decreased greatly. Since industrial wastewaters such as the one examined in this study contain a complex combination of chemicals, the ClO_2 catalytic oxidation process is hopeful to be used in degradation of various organic contaminants and industrial effluents. Further investigation is in progress.

4. Conclusions

In conclusion, this study reports the results for the degradation of DNBP by ClO_2 oxidation process with Al_2O_3 as catalyst. Al_2O_3 exhibits an excellent catalytic activity in the ClO_2 catalytic oxidation process so that almost complete removal efficiency (99.1%) of 39 mg L^{-1} of DNBP wastewater can be achieved through treatment for 60 min in the pH 4.66 by adding 10.7 g L^{-1} and 0.355 g L^{-1} of Al_2O_3 catalyst and ClO_2 , respectively. The kinetic studies revealed that the ClO_2 catalytic oxidation degradation of DNBP followed pseudo-first-order kinetics with respect to DNBP concentration. A good linear relationship existed between the obtained rate constant k and the initial concentration of ClO_2 and DNBP, respectively. No obvious decline in efficiency of the catalyst was observed after 8 repeated cycles and this made the application of ClO_2 catalytic oxidation process for degrading organic pollutants from aqueous solution more practical.

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