Catalytic ozonation of acid red 18 wastewater using $\text{Ca}(\text{OH})_2$ as catalyst in a micro bubble gas-liquid reactor

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ABSTRACT

The ozonation of acid red 18 (AR18) wastewater was investigated in an integrated process consisting of $\text{O}_3/\text{Ca}(\text{OH})_2$ system and a newly-developed micro bubble gas-liquid reactor. The effects of operating parameters such as $\text{Ca}(\text{OH})_2$ dosage, reactor pressure, liquid phase temperature, initial dye concentration and inlet ozone concentration on decolorization and mineralization (TOC removal) were studied in order to know the ozonation performance of this new integrated process. The decolorization and TOC removal efficiency increased with increasing inlet ozone concentration and increasing $\text{Ca}(\text{OH})_2$ dosage before 2 g/L, as well as decreasing initial dye concentration. The optimum $\text{Ca}(\text{OH})_2$ dosage should exceed $\text{Ca}(\text{OH})_2$ solubility in liquid phase. The reactor pressure and liquid phase temperature have little effects on the decolorization and TOC removal efficiency. When $\text{Ca}(\text{OH})_2$ dosage exceeded 3 g/L, the decolorization and TOC removal of AR 18 almost reached 100 % at 6 and 25 min., respectively. The intensification mechanism of $\text{Ca}(\text{OH})_2$ catalytic ozonation was explored through the determination of CO_3^{2-} and SO_4^{2-} ions formed in the liquid phase and analysis of the precipitated substances. The mechanism for $\text{Ca}(\text{OH})_2$ intensified mineralization of dye solution is the simultaneous removal of CO_3^{2-} ions, as hydroxyl radical scavengers, due to the presence of Ca^{2+} ions. Results indicated that the proposed new integrated process is a high efficient ozonation process for persistent organic wastewater treatment.

Keywords: decolorization; mineralization; ozonation; dye wastewater

1. Introduction

Dyes are synthetically aromatic compounds which are used in variety of industries such as textile, pharmaceutical, pulp and paper, paint, plastic, food and electroplating [1]. The textile industry generates large amount of effluents which contain a large quantity of unconsumed dye in it. For example, azo dyes that have one or more azo

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bonds are widely used as commercial reactive dyes [1]. It is estimated that about 10~15 % of weight of the dye is lost in the dyeing process and constitutes the major organic pollutants of the effluent [2]. Since most of dye compounds are toxic, recalcitrant and chemically and photo-chemically stable, their effect on environment has been a matter of concern for public and governments at all levels [3].

It has been proved that neither simple chemical methods nor biological treatment can result in desired removal of color and depletion of COD [2]. A direct alternative to solve this problem is treatment by chemical oxidation. Advanced oxidation processes (AOPs) are considered to be promising methods for the treatment of hazardous toxic organic pollutants in wastewater. In AOPs highly reactive hydroxyl radicals are produced, which can oxidize majority of organic pollutants in wastewater unselectively [4]. Ozonation is one of the AOPs which is used to degrade organic pollutants effectively from wastewater, such as pesticides, dyes and herbicides and even biorecalcitrant chemical species that resist biological treatment [3].

Depending on the pH of liquid phase, ozone may react with a large number of organic compounds by direct oxidation or by indirect oxidation through formation of secondary oxidants like hydroxyl radicals [5]. Based on their standard oxidation potentials, hydroxyl radicals are stronger oxidants than molecular ozone. In O_3/OH^- system, the hydroxide ions react with ozone to yield superoxide anion radicals ($\cdot O_2^-$), which in turn are involved in a series of chain reactions, producing hydroxyl radicals. Overall 1 mol of hydroxyl radicals needs 1.5 mol of O_3 to produce it [6,7]. So for wastewater treatment, the consumption of ozone is usually high. Up on mineralization of organic pollutants at elevated pH, HCO_3^- and CO_3^{2-} ions are formed, which act as radical scavengers [3,8], thus lowering the indirect reaction rate. On the contrary, at low pH values acidic compounds may be formed which are resistant to further ozonation. As a consequence, the total consumption of ozone is usually high for complete mineralization, resulting in high operation cost [8].

Considering these disadvantage of ozonation, ozone is often used in combination with other technologies such as H_2O_2 , UV, TiO_2 and electro-peroxone (E-peroxone) in dye wastewater treatment [9-12]. In these combination processes, H_2O_2 , UV, and TiO_2 catalyze ozone to produce more hydroxyl radicals, improving pollutant mineralization efficiency. In order to simultaneously remove HCO_3^- and CO_3^{2-} radical scavengers at elevated pH, we suggested a patented $O_3/Ca(OH)_2$ system, greatly improving ozonation efficiency of organic pollutants in wastewater [13]. In this new catalytic

67 ozonation, Ca(OH)_2 in aqueous solution ionize into Ca^{2+} and OH^- ions, the former
68 could react with HCO_3^- and CO_3^{2-} ions to form CaCO_3 and the latter could constitute
69 O_3/OH^- system. This two processes coupled each other to promote the catalytic
70 ozonation of organic pollutants.

71 The industrial application of ozonation have been limited by high production
72 cost of ozone and the low ozone utilization due to poor mass transfer rate of ozone
73 [14]. It has been reported that the rate-limiting-step in the ozonation of dye-containing
74 wastewater is the mass transfer of ozone from the gas phase to the liquid phase owing
75 to its low solubility in water [15-18]. The mass transfer of ozone in some
76 conventional gas-liquid reactors such as bubble columns [19] and fluidized bed
77 reactors [20], is also limited because of smaller specific surface area and lower partial
78 pressure of ozone. In order to intensify the mass transfer rate of ozone, some new
79 ozonation reactors such as hollow fiber membrane reactor [21,22], micro porous
80 tube-in-tube microchannel reactor [23], and hierarchical porous ceramic membrane
81 reactor [24], have been developed in recent years. All these new reactors exhibited
82 excellent ozonation performance compared with the conventional reactors because of
83 the improvement of ozone mass transfer rate.

84 In our group, we developed a new high efficient ozonation reactor that used a
85 gas-liquid mixing pump to realize the compulsory mixing of ozone and wastewaters.
86 The gas-liquid mixing pump could disperse ozone phase into numerous micro gas
87 bubbles with microscale, thus increasing the gas-liquid phase interface largely and
88 ozone equilibrium concentration in liquid phase because of the large partial pressure
89 in the micro gas bubbles. As a result, the gas-liquid mixing pump intensified largely
90 the mass transfer of ozone from gas phase to liquid phase. Therefore, the aim of this
91 work is to investigate the ozonation performance of acid red 18 wastewater in a new
92 integrated process including the patented $\text{O}_3/\text{Ca(OH)}_2$ system and the micro bubble
93 gas-liquid reactor, and thus providing a new idea of catalytic ozonation of organic
94 pollutants in wastewater. The influences of major parameters such as Ca(OH)_2 dosage,
95 system pressure, inlet ozone concentration and initial AR 18 concentration on the
96 decolorization and mineralization of AR 18 have been investigated, and the
97 intensification mechanism of Ca(OH)_2 was also explored.

99 2. Experimental

100 2.1 Reagents

Commercial AR 18 dye was purchased from a chemical reagent company (adamas-beta, Switzerland) and used without further purification. The most important physical and chemical properties of this reactive dye are as follows: molecular mass 604.47 g/mol, purity 85%, water solubility 20 g/L and maximum absorption 510 nm. Other chemicals such as $\text{Ca}(\text{OH})_2$ 、 NaOH 、 H_2SO_4 were of analytical grade. The dye solution was prepared by dissolving AR 18 in deionized water, and the natural pH of the dye solution with 450 mg/L AR 18 was about 8. The initial pH of the dye solutions were adjusted using 1 M H_2SO_4 and 1 M NaOH solution.

2.2 Experimental setup and procedures

All the experimental setup includes a micro bubble ozonation reactor, a gas-liquid mixing pump (25QY-2DS, Southern pump Ld. Co., micro gas bubbles with diameter of 20~30 μm could be produced in this pump reported by the manufacturer.), an ozone generator (HBO3-20, Beijing 322 water equipments Ld. Co.), a liquid tank and other detection devices, and its schematic diagram is shown in Fig. 1. The reactor is an acrylic tube reactor with diameter of 70 mm and length of 900 mm, and is connected with the gas-liquid mixing pump. A Teflon tube wire that could supply about 0.53m^2 of heat transfer area, is placed in the liquid tank to adjust the temperature of reaction system. Ozone was produced from pure oxygen by the ozone generator, its flow rate into the pump mixer was controlled using a gas flow meter, and its inlet concentration was detected by an ultraviolet ozone detector (JSA9-03-UV, Shengzheng Jishunan Science and Technology Ld. Co.) amounted on the by-pass line. The ozone-oxygen mixture stream from the ozone generator was sucked into the gas-liquid mixing pump to produce micro gas bubbles in the dye wastewater, and then the two-phase mixture flowed into the ozonation reactor. After ozonation in the reactor, the two phase mixture flowed out from the reactor top and flowed into the liquid tank for gas and liquid separation and the gas phase subsequently flowed into the exhausted gas discharge pipe system with an ultraviolet ozone detector. Liquid samples were collected from the sampling tube inserted into the liquid tank. The liquid recirculation flow rate and the pressure of the reaction system were controlled by a ball valve amounted on the outlet pipe of the reactor.

In every run, 8 L of the dye solution was used. During all the experiments, the water used to prepare dye solution was distilled water, but for the mechanism

experiment the used water was ultrapure water. The ozone concentration in the inlet gas stream was monitored by the ozone analyzer, and the gas stream was not fed into the reactor until the a desired ozone concentration was achieved. 40 ml of each liquid sample was collected from the sampling tube, and then was centrifuged at 3000 rpm to get supernatant and then the supernatant was vacuum filtered to get clear liquid sample for the determination of AR 18 concentration and total organic carbon (TOC).

2.3 Analytical methods

AR18 concentration in wastewater was determined using a UV-Vis spectrophotometer (TU-1901, Beijing Puxi analyzing devices Ld. Co. ,China) at AR 18 maximum absorption wavelength of 510 nm. The decolorization efficiency was calculated in terms of the initial AR 18 concentration and AR 18 concentration after ozonation.

TOC reduction could be considered as an indicator of mineralization of organic pollutants in wastewater. The TOC in the wastewater was detected using a TOC analyzer (TOC-LCPH, Shimadzu, Japan). The TOC removal efficiency was calculated in terms of the initial TOC and TOC after ozonation.

The concentration of SO_4^{2-} and CO_3^{2-} ions before and after ozonation of wastewater was measured by an ion chromatograph (ICS-600, shanghai Daian analyzing devices Lt. Co., China). 10 μL of the sample was pre-filtered by passing through a C18 solid-phase extraction (SPE) column and injected into a separation column (IonPac AS23, 250 mm ,4.0 mm) for analysis. The eluent was KOH (20 mM) with a flow rate of 1 mL/min.

In order to explore the mechanism of $\text{Ca}(\text{OH})_2$ intensified ozonation, the solid phase substances before and after ozonation of the wastewater were sampled, and vacuum dried at 110°C . The diffraction pattern of the solid samples was recorded by an X-ray diffract meter (XRD-6000, Shimadzu, Japan). The X-ray diffraction conditions: Cu target and a conventional slit system (namely, the divergence slit DS = the scattering slit SS = 1° , reception slit = 0.3 mm), scanning range $10\sim 80^\circ$, scanning speed $5^\circ/\text{min}$ and sampling interval 0.02 degrees.

3. Results and discussion

3.1 Catalytic effect of $\text{Ca}(\text{OH})_2$ on ozonation of AR 18

The catalytic effect of $\text{Ca}(\text{OH})_2$ on the decolorization and TOC removal of AR 18

wastewater was investigated and the results were shown in Fig. 2. It could be seen that in the presence of Ca(OH)_2 , the degradation and mineralization processes of AR 18 were obviously accelerated, leading to the highest decolorization and TOC removal efficiencies among the O_3 , Ca(OH)_2 and $\text{O}_3/\text{Ca(OH)}_2$ processes. It is especially worthy of noting that alone Ca(OH)_2 has little effect on the mineralization of degradation products of AR 18, whereas $\text{O}_3/\text{Ca(OH)}_2$ system could reach almost 100 % of the TOC removal at about 25 min. compared with the lower TOC removal efficiency for the simple ozonation process. Therefore, Ca(OH)_2 exhibited excellent catalytic effect on ozonation process of dye wastewater.

3.2 Effect of process parameters on decolorization and mineralization of AR 18

3.2.1 Effect of Ca(OH)_2 dosage

The effects of Ca(OH)_2 dosage on the decolorization and TOC removal efficiency of AR 18 wastewater were first investigated because of the importance of solution pH value and Ca^{2+} concentration in ozonation process, as mentioned above. Fig.3 displays the variation process of the removal efficiencies and pH change of the liquid phase with ozonation time at Ca(OH)_2 dosage of 0~3 g/L. It could be seen that the decolorization and TOC removal efficiencies all increased with Ca(OH)_2 dosage before the dosage of 2 g/L, after that the effect of Ca(OH)_2 dosage was not obvious. It seems that the optimum Ca(OH)_2 dosage should exceed Ca(OH)_2 solubility in liquid phase. As shown in Fig. 3, this may be explained by the fact that only sufficient Ca(OH)_2 could release enough Ca^{2+} and OH^- ions to maintain the high pH value and to remove HCO_3^- and CO_3^{2-} radical scavengers at elevated pH which are formed due to the mineralization of dye degradation products.

It was also observed that the time for decolorization was shorter than that for TOC removal, and in comparison, Ca(OH)_2 dosage had a more obvious effect on TOC reduction than on decolorization. In ozonation, ozone molecules rapidly and selectively attack unsaturated bond of chromophores resulting a rapid removal of color [25-27], but ozonation by-products such as organic acids, aldehydes and ketones, cannot be oxidized by ozone molecules easily [28-31]. With the increasing of Ca(OH)_2 dosage, the pH value of the dye solution also increased and reached the saturated pH value of Ca(OH)_2 finally. It is well known that ozone is able to form a more powerful, non-selective hydroxyl radicals at high pH values [32]. Therefore, when Ca(OH)_2 dosage exceeded its solubility in wastewater, excessive Ca(OH)_2 could

maintain the highest pH value of the liquid phase and make ozone produce more powerful hydroxyl radicals, resulting the further mineralization of the ozonation by-products and higher TOC reduction efficiency in a shorter time period (about 25 min. in this experiment). Certainly, the possibility that the Ca^{2+} ions in the dye solution could react with the radical scavengers, HCO_3^- and CO_3^{2-} to form CaCO_3 may be another important factor to accelerate the mineralization of ozonation by-products. But this needs to be further verified as mechanism discussion.

3.2.2 Effect of reactor pressure

In this newly developed ozonation process, the ozone-oxygen mixture gas and the dye solution were simultaneously sucked by the gas-liquid pump mixer in which the gas phase was compulsorily dispersed into numerous micro gas bubbles, and the gas-liquid mixture was then pushed into the reactor. Thus pressure in the reactor may affect the dispersion and agglomeration state of the micro gas bubbles, which in turn may affect ozone mass transfer between the two phases. So as an important parameter, the effect of reactor pressure on the decolorization and TOC removal efficiency of AR 18 wastewater was investigated, as shown in Fig. 4. It was found that the reactor pressure has little effect on the decolorization and TOC removal efficiency in the pressure range of 0.05~0.35 MPa. Increasing the pressure could increase the partial pressure of ozone, thus facilitating the mass transfer of ozone from gas phase to the liquid phase. But this effect was not observed from the kinetics curves. As mentioned above, the rate-limiting-step in the ozonation of dye-containing wastewater is the mass transfer of ozone owing to its low solubility in water [15-18]. So this phenomenon indicated that increasing the reactor pressure has not obvious effect on the mass transfer of ozone. A possible explanation for this phenomenon is that the internal pressure in the micro gas bubbles is much larger than their external pressure, and the internal pressure dominates the mass transfer of ozone. Therefore, in our new ozonation reactor, the mass transfer of ozone should have been intensified largely by the gas-liquid pump mixer. This may be further explained by the fact that the large partial pressure of ozone in the micro gas bubbles significantly increased the driving force of ozone mass transfer, and on the other hand the numerous micro gas bubbles increased the mass transfer area between the two phases.

3.2.3 Effect of liquid phase temperature

Reaction temperature will significantly influence the solubility and stability of ozone in water [33], which may influence the ozonation efficiency. The effect of liquid phase temperature on color and TOC removal was investigated at 25~40°C. As is shown in Fig. 5, when the temperature was increased from 25°C to 40°C, the difference of color removal rate was not remarkable, and only the TOC removal rate was slight different but not obvious. Generally speaking, increasing liquid phase temperature will decrease the solubility of ozone and reduce the mass transfer rate of ozone from gas phase into liquid phase, which has adverse impact on dye degradation. However, this study indicated that liquid temperature has not obvious effect on both TOC and color removal. Hu et al. [34] obtained a similar result in their work on catalytic ozonation and gave a possible reason for this result. Although increasing the liquid phase temperature depressed the mass transfer of ozone, the oxidation rate of ozonation was accelerated significantly.

3.2.4 Effect of initial dye concentration

The effect of initial AR 18 concentration on color and TOC removal rate was also carried out to explore the feasibility of this ozonation process for different concentrations of dye wastewaters. As is illustrated in Fig. 6, higher color and TOC removal rate was much easier to obtain in the process that adopted a lower concentration of dye solution. As the initial dye concentration increased from 300 mg/L to 750 mg/L, the difference of color and TOC removal was obvious before about 10 min and 35 min, respectively, but after that time the color and TOC removal reached almost a same level.

When more concentrated dye solution was used, the ratios of ozone molecules to dye molecules in the solution decreased and more ozone was consumed [35,36]. And also, more various intermediates from degradation of the parent dye would be formed in a higher concentration of dye solution, leading to more pronounced suppression effect on the oxidation [37,38]. Thus, the time for complete decolorization and TOC removal would be longer for higher initial dye concentrations [32,34]. However, in current $O_3/Ca(OH)_2$ system, the time for complete color and TOC removal of different concentrations of dye solutions was almost the same, indicating a higher ozone utilization efficiency. The reason for this result may be the simultaneous removal effect of mineralization products by the Ca^{2+} in the dye solution.

3.2.5 Effect of inlet ozone concentration

The effect of inlet ozone concentration on decolorization and TOC removal of AR 18 solution is shown in Fig. 7. Increasing the ozone dosage from 30 to 75 mg/L increased the rate of color and TOC removal. It is clearly shown that the color and TOC removal rates were significantly affected by the inlet ozone concentration, and especially for the TOC removal rate. The fact that an increase in the inlet ozone concentration increases both the dye and TOC removal was verified by other researchers [32,34,39]. There are about two possible explanations, one is the increased ozone dosage per volume of dye solution [32], and the other is the increasing of both mass transfer driving force and ozone-derived free radicals due to the increase of inlet ozone concentration [34]. It was also observed that ozone dose above 65 mg/L did not show any noticeable increase in dye and TOC removal. A similar result was obtained by Tehrani-Bagha et al. [32]. As mentioned above, the rate-limiting-step in the ozonation of dye-containing wastewater is the mass transfer of ozone owing to its low solubility in water [15-18]. So when ozone inlet concentration exceeds a critical value, the rate-limiting-step would turn into a kinetically controlled regime. Certainly, the critical ozone value should depend on the type of dye or its molecular structure.

3.2.6 Effect of ozone flow rate

The effect of ozone flow rate on decolorization and TOC removal of AR 18 solution is shown in Fig. 8. The rates of color and TOC removal were increased with the increase of ozone flow rate before 3 L/min, but after that the rates did not have obvious change. As mentioned above, the rate-limiting-step in the ozonation of dye-containing wastewater is the mass transfer of ozone. Under a certain ozone concentration and a certain initial dye concentration of AR 18, increasing ozone flow rate means the increase of ozone dosage in a same period of ozonation time, and thus accelerating the ozonation process. However, when the input rate of ozone to the liquid phase exceeded that consumed by the ozonation reactions, continuing the increase of ozone flow rate did not have obvious effects on decolorization and TOC removal efficiencies because the rate-limiting-step would turn into a kinetically controlled regime.

3.3 Mechanism of Ca(OH)₂ intensified mineralization

In order to explore the mechanism of Ca(OH)₂ intensified mineralization of AR 18, a series of UV-Vis spectra of liquid samples taken at different time were scanned and the results were shown in Fig. 9. It could be seen that the maximum absorption peak of AR 18 at about 510 nm first disappeared and the absorption peaks between 200 nm and 250 nm disappeared at last. This fact illustrated that AR 18 was first broken down at its chromophore site, producing various small molecules with benzene rings, and these small aromatic compounds were finally mineralized. All the absorption peaks of the liquid samples in the presence of 3 g/L Ca(OH)₂ disappeared more quickly than that without Ca(OH)₂, but the change process of all the absorption peaks was similar. This indirectly indicated that the presence of Ca(OH)₂ did not change the chemical paths of degradation and mineralization of AR 18.

As mentioned above, Ca(OH)₂ in dye solution would ionize to form Ca²⁺ and OH⁻ ions. It is well known that OH⁻ ions will form O₃/OH⁻ system, which produces high reactive hydroxyl radicals. Compared with other O₃/OH⁻ system in higher pH solution, the difference of current O₃/OH⁻ system is the presence of rich Ca²⁺ ions in solution. So it is apparent that the intensification mechanism of Ca(OH)₂ catalytic ozonation should be explored from the effect of Ca²⁺ ions. In order to understand this effect, two ozonation experiments were designed using NaOH and Ca(OH)₂ as pH adjuster, respectively. As shown in Fig. 10a, the TOC removal rate using Ca(OH)₂ as catalyst is much higher than that with NaOH as catalyst, and this difference becomes more and more obvious as the ozonation time increases. For example, the TOC removal for O₃/NaOH system was about 43 % at 35 min of ozonation time, whereas the TOC removal for O₃/ Ca(OH)₂ system was more than 98 % at 25 min of ozonation time. And at the same time, the CO₃²⁻ concentration determined using I.C. is much lower for O₃/ Ca(OH)₂ system than that for O₃/NaOH system. So where the CO₃²⁻ ions went should be related with the intensification mechanism of dye mineralization.

The variation of SO₄²⁻ concentration and TOC removal is shown in Fig. 10b. It could be seen that the SO₄²⁻ concentration as a mineralization product is higher for O₃/ Ca(OH)₂ system before 25 min but then becomes lower than that for O₃/NaOH system after 30 min of ozonation time. This may be explained by the faster TOC removal rate which in turn resulted in faster increase of SO₄²⁻ ions before 25 min. and then the SO₄²⁻ may be consumed by the Ca²⁺ ions to form CaSO₄ in O₃/ Ca(OH)₂ system.

As discussed above, in the $O_3/ Ca(OH)_2$ system, it was expected that CO_3^{2-} ions as the scavengers of hydroxyl radicals would be removed simultaneously due to the presence of Ca^{2+} ions, thus enhancing the efficiency of ozonation. If so, the formed product $CaCO_3$ should exist in the precipitated substances in the $O_3/ Ca(OH)_2$ system. As shown in Fig. 11. the diffraction pattern of the precipitated substances displayed the presence of $CaCO_3$ and $CaSO_4$. This verified that the CO_3^{2-} and SO_4^{2-} ions were precipitated by the Ca^{2+} ions in the new $O_3/ Ca(OH)_2$ system, and this should be the mechanism of $Ca(OH)_2$ intensified mineralization of dye wastewater.

4. Conclusions

In this paper, an integrated process consisting of a patented $O_3/Ca(OH)_2$ system and a newly-developed micro bubble gas-liquid reactor was proposed to enhance the catalytic ozonation of Acid Red 18 wastewater. The intensification mechanism of $Ca(OH)_2$ catalytic ozonation was explored through the determination of CO_3^{2-} and SO_4^{2-} ions formed in the $O_3/Ca(OH)_2$ system and X-ray diffraction analysis of the precipitated substances.

Increasing inlet ozone concentration before 75 mg/L, ozone flow rate before 3 L/min and $Ca(OH)_2$ dosage before 2 g/L, as well as decreasing initial dye concentration, would increase the decolorization and TOC removal efficiency. The optimum $Ca(OH)_2$ dosage should exceed $Ca(OH)_2$ solubility in liquid phase. The reactor pressure and liquid phase temperature have little effects on the decolorization and TOC removal efficiency. The reason for $Ca(OH)_2$ intensified mineralization of the dye solution is the simultaneous removal of hydroxyl radical scavengers- CO_3^{2-} ions due to the presence of Ca^{2+} ions.

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References

- [1] J.Basin Parsa, M.Rezaei, A.R.Soeymani, Electrochemical oxidation of an azo dye in aqueous media investigation of operational parameters and kinetics, J. Hazard. Mater. 168 (2009) 997-1003.

- [2] H.W.Chen, Y.L.Kuo, C.S.Chiou, S.W.You, M.C.Ma, C.T.Chang, Mineralization of reactive black 5 in aqueous solution by ozone/H₂O₂ in the presence of magnetic catalyst, J. Hazard. Mater. 174 (2010) 795-800.
- [3] J.Basiri Parsa, S.Hagh Negahdar, Treatment of wastewater containing Acid blue 92 by advanced ozone-based oxidation methods, Sep. Purif. Technol. 98 (2012) 315-20.
- [4] H.Kusic, N.Koprivanac, A.L.Bozic, Minimization of organic pollutant content in aqueous solution by means of AOPs, UV and ozone based technologies, J. Chem. Eng. 123 (2006) 127-137.
- [5] S.Baig, P.A.Liechit, Ozone treatment for biorefractory COD removal, Water Sci. Technol. 43 (2) (2001) 197-204.
- [6] D.M.Bila, A.F.Montalvao, A.C.Silva, M.Dezotti, Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement, J. Hazard. Mater. 117 (2~3) (2005) 235~242.
- [7] C.Tizaoui, L.Bouselmi, L.Mansouri, A.Ghrabi, Landfill leachate treatment with ozone and ozone/hydrogen peroxide system, J. Hazard. Mater. 140 (1-2) (2007) 316-324.
- [8] P.V. Aken, N.Lambert, J.Degreve, S.Liers, J.Luyten, Comparison of different oxidation methods for recalcitrance removal of landfill leachate, Ozone Sci. Eng. 33 (2011) 294-300.
- [9] H.J.Hsing, P.C.Chiang, E.E.Chang, M.Y.Chen, The decolorization and mineralization of Acid Orange 6 azo dye in aqueous solution by advanced oxidation processes: a comparative study, J. Hazard. Mater. 141(1) (2007) 8-16.
- [10] H.Y.Shu, Degradation dyehouse effluent containing CI Direct Blue 199 by processes of ozonation, UV/H₂O₂, and in sequence of ozonation with UV/H₂O₂, J. Hazard. Mater. 133(1-3) (2006) 92-98.
- [11] A.Lopez, H.Benbelkacem, H.Debellefontaine, Oxidation pathways for ozonation of azo dyes in a semi-batch reactor: A kinetic parameters approach, Environ. Technol. 25(3) (2004) 311-321.
- [12] B.Bakheet, S.Yuan, Z.Li, H.Wang, J.Zuo, K.Sridhar, Y.Wang, Electro-peroxone treatment of orange II dye wastewater, Water Res. 47 (2013) 6234-6243.
- [13] Y.Yan, X.Quan, Z.Cheng, F.Xu, F.Qiu, Catalytic ozonation of biologically treated leachate from municipal solid waste incineration power plant, Chinese J. Environ. Eng. 9 (2015) 219-224.
- [14] A.H.Konsowa, M.E.Ossman, Y.Chen, J.C.Crittenden, Decolorization of industrial wastewater by ozonation followed by adsorption on activated carbon, J.Hazard.Mater, 176 (2010) 181-185.

408 [15] F.M. Saunders, J.P.Gould, C.R.Southerland, The effect of solute competition on ozonolysis of
 409 industrial dyes, *Water Res.* 17(1983) 1407-1419.

410 [16] H.Y. Shu, C.R Huang, Degradation of commercial azo dyes in water using ozonation and UV
 411 enhanced ozonation process, *Chemosphere*, 31 (1995) 3813-3825.

412 [17] J. Carriere, Decolorization of textile dye solutions. *Ozone Science and Eng.* 3(2008)
 413 189-200.

414 [18] C.Lin, W. Liu, Ozone oxidation in a rotating packed bed, *J. Chem. Technol. Biotechnol.* 78
 415 (2003) 138-141.

416 [19] A.Gabelman, S.T.Hwang, Hollow fiber membrane contactors, *J. Membr. Sci.* 159 (1999)
 417 61-106.

418 [20] F.Tisa, A.A.A. Raman, M.A.W.D. Wan, Applicability of fluidized bed reactor in recalcitrant
 419 compound degradation through advanced oxidation processes: A review. *J. Environ manage.*
 420 146(2014) 260-275.

421 [21] H.Zhang, M.Jiang, D.Zhang, Q.Xia, Decomposition of 4-nitrophenol by ozonation in a
 422 hollow fiber membrane reactor. *Chem. Eng. Comm.* 197 (2010) 377-386.

423 [22] S.Bamperng, T.Suwannachart, S.Atchariyawut, R.Jiratananon, Ozonation of dye
 424 wastewater by membrane contactor using PVDF and PTFE membranes, *Sep. Purif. Technol.*
 425 72(2010)186-193.

426 [23] M.Gao, Z.Zeng, B.Sun, H.Zou, J.Chen, L.Shao, Ozonation of azo dye Acid 14 in a
 427 microporous tube-in-tube microchannel reactor: Decolorization and mechanism,
 428 *Chemosphere*, 89 (2012) 190-197.

429 [24] Y.Zhu, S.Chen, Q.Xie, Y.Zhang, C.Gao, Y.Feng, Hierarchical porous ceramic membrane with
 430 energetic ozonation capability for enhancing water treatment, *J. Membr. Sci.* 431(2013)197
 431 - 204.

432 [25] O.Salome, G.P.Souares, J.M.Orfao, D.Portela, A.Vieira, M.Fernando, R.Pereira, Ozonation of
 433 textile effluents and dye solutions under continuous operation: Influence of operating
 434 parameters, *J. Hazard. Mater.* 137(2006)1664-1673.

435 [26] E.Acar, T.Ozbelge, Oxidation of Acid Red-151 aqueous solutions by the peroxone process
 436 and its kinetic evaluation, 28(2006)155-164.

437 [27] S.Pirgaloğlu, T.A.Özbelge, Comparison of non-catalytic and catalytic ozonation processes of
 438 three different aqueous single dye solutions with respect to powder copper sulfide catalyst,
 439 *Appl. Catal. A: General*, 363(2009)157-163.

440 [28] OSGP. Soares, PCC.Faria, JJM.Órfão, MFR.Pereira, Ozonation of textile effluents and dye
 441 solutions in the presence of activated carbon under continuous operation, *Sep. Purif.*

Technol.42 (2007)1477-1492.

- [29] M.Hassan, C.J.Hawkyard, Decolourisation of dyes and dyehouse effluent in a bubble - column reactor by heterogeneous catalytic ozonation, J. Chem. Technol. Biotechnol. 81(2006)201-207.
- [30] F.Erol, T. A. Ozbelge, Catalytic ozonation with non-polar bonded alumina phases for treatment of aqueous dye solutions in a semi-batch reactor, Chem. Eng. J. 139(2008)272-283.
- [31] B.K.Hordern, M.Zi ótek, J.Nawrocki, Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment, Appl. Catal. B. Environ. 46(2003)639-669.
- [32] A.R.Tehrani-Bagha, N.M.Mahmoodi, F.M.Menger, Degradation of a persistent organic dye from colored textile wastewater by ozonation, Desalination, 260(2010)34-38.
- [33] A.C. Gomes, J.C. Nunes, R.M.S.Simoes, Determination of fast ozone oxidation rate for textile dyes by using a continuous quench-flow system. J. Hazard. Mater. 178(2010)57-65.
- [34] E. Hu, X. Wu, S. Shang, X. Tao, S. Jiang, L. Gan, Catalytic ozonation of simulated textile dyeing wastewater using mesoporous carbon aerogel supported copper oxide catalyst. J. Clean Prod. 112(2016)4710-4718.
- [35] E. Oguza, B. Keskinler, C. Celik, Z. Celik, Determination of the optimum conditions in the removal of Bomaplex Red CR-1 dye from the textile wastewater using O_3 , H_2O_2 , HCO_3^- and PAC, J.Hazard. Mater. 131(2006)66-72.
- [36] M.F. Sevimli, C. Kinaci, Decolorization of textile wastewater by ozonation and Fenton's process, Water Sci. Technol. 45 (2002)279-286.
- [37] N.M. Mahmoodi, M. Arami, Bulk phase degradation of Acid Red 14 by nanophotocatalysis using immobilized titanium (IV) oxide nanoparticles, J. Photochem. Photobiol. 182 (2006) 60-66.
- [38] N.M. Mahmoodi, M. Arami, N.Y. Limaee, K. Gharanjig, F.D. Ardejani, Decolorization and mineralization of textile dyes at solution bulk by heterogeneous nanophotocatalysis using immobilized nanoparticles of titanium dioxide, Colloid Surface. 290(2006)125-131.
- [39] F. Gholami-Borujeni, K. Naddafi, F. Nejatade-Barandozi, Application of catalytic ozonation in treatment of dye from aquatic solution. Desalin. Water Treat. 51(2013)6545-6551.

Figure captions

Fig. 1 Experimental setup. 1. Ozone generator; 2. Gas-liquid mixing pump; 3. Tube ozonation reactor; 4. Pressure gauge; 5. Ball valve; 6. Liquid flow meter; 7. Liquid tank; 8. Liquid inlet pipe; 9,13,15. Valves; 10. Exhausted gas dryer; 11,17. Ozone detector; 12,18. Exhausted gas absorption equipment; 14,16. Gas flow meter.

Fig. 2 Catalytic effect of $\text{Ca}(\text{OH})_2$ on color, TOC removal of AR 18: ozone inlet flow rate 3.5 L/min; ozone inlet concentration 65 mg/L; initial AR 18 concentration 450 mg/L and TOC 145 mg/L; ozonation reactor pressure 0.35 MPa; $\text{Ca}(\text{OH})_2$ dosage 3 g/L; liquid phase temperature 25 °C.

Fig. 3 Effect of $\text{Ca}(\text{OH})_2$ dosage on color, TOC removal efficiency of AR 18 and pH change of liquid phase: ozone inlet flow rate 3.5 L/min; ozone inlet concentration 65 mg/L; initial AR 18 concentration 450 mg/L and TOC 145 mg/L; ozonation reactor pressure 0.35 MPa; liquid phase temperature 25 °C.

Fig. 4 Effect of reactor pressure on color and TOC removal efficiency of AR 18: ozone inlet flow rate 3.5 L/min; ozone inlet concentration 65 mg/L; initial AR 18 concentration 450 mg/L and TOC 145 mg/L; $\text{Ca}(\text{OH})_2$ dosage 3 g/L; liquid phase temperature 25 °C.

Fig. 5 Effect of liquid phase temperature on color and TOC removal efficiency of AR 18: ozone inlet flow rate 3.5 L/min; ozone inlet concentration 65 mg/L; initial AR 18 concentration 450 mg/L and TOC 145 mg/L; $\text{Ca}(\text{OH})_2$ dosage 3 g/L; ozonation reactor pressure 0.35 MPa.

Fig. 6 Effect of initial dye concentration on color and TOC removal efficiency of AR 18: ozone inlet flow rate 3.5 L/min; ozone inlet concentration 65 mg/L; $\text{Ca}(\text{OH})_2$ dosage 3 g/L; ozonation reactor pressure 0.35 MPa; liquid phase temperature 25 °C.

Fig. 7 Effect of inlet ozone concentration on color and TOC removal efficiency of AR 18: ozone inlet flow rate 3.5 L/min; initial AR 18 concentration 450 mg/L and TOC 145 mg/L; $\text{Ca}(\text{OH})_2$ dosage 2 g/L; ozonation reactor pressure 0.35 MPa; liquid phase temperature 25 °C.

Fig. 8 Effect of ozone flow rate on color and TOC removal efficiency of AR 18: ozone concentration 65 mg/L; initial AR 18 concentration 450 mg/L and TOC 145 mg/L; $\text{Ca}(\text{OH})_2$ dosage 3 g/L; ozonation reactor pressure 0.35 MPa; liquid phase temperature 28 °C.

Fig. 9 UV-Vis spectra of liquid phase samples during the ozonation of AR 18: ozone inlet flow rate 3.5 L/min; initial AR 18 concentration 450 mg/L and TOC 145 mg/L; ozone concentration 65 mg/L; ozonation reactor pressure 0.35 MPa; liquid phase temperature 28 °C.

Fig. 10 Variation of CO_3^{2-} , SO_4^{2-} ions concentration and TOC removal rate during the ozonation of AR 18: ozone inlet flow rate 3.5 L/min; initial AR 18 concentration 450 mg/L and TOC 145 mg/L; ozone concentration 50 mg/L; ozonation reactor pressure 0.35 MPa; liquid phase temperature 25 °C; pH values 12.55 and $\text{Ca}(\text{OH})_2$ dosage 2 g/L.

Fig. 11 The diffraction pattern of the precipitated substances in $O_3/ Ca(OH)_2$ system

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