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Determination of ozone adsorption in activated sludge system and its effect on sludge properties

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ABSTRACT

In this study, the amount of ozone which is adsorbed by the activated sludge system and the effect of ozonation on the sludge properties were investigated. Two batch reactors, one control and one ozonated were used. During the test, the ozonation time was increased from 15 to 185 s, the ozone concentration was 0.73–4.83 $mgO_3\,g^{-1}$ MLSS and the mixed liquid suspended solid (MLSS) was 11–14 $g\,L^{-1}$. In an ozonated reactor, with increasing the ozonation time the ozone concentration was determined in order to calculate how much ozone adsorbed in sludge system. It was found that the ozone concentration increased in the activated sludge system with time and after it reached to the maximum level in 40 s, it decreased. Based on the result, MLSS was not affected by ozonation. When ozone dose was less than 3.8 $mgO_3\,g^{-1}$ MLSS, soluble chemical oxygen demand (SCOD) decreased or did not change but while applying dosages higher than 3.8 $mgO_3\,g^{-1}$ MLSS, SCOD increased. In addition, protein and polysaccharide which are the main parameter in fouling in membrane bioreactors decreased when ozone dosage was less than 3.8 $mgO_3\,g^{-1}$ MLSS while they increased when ozone dose is higher than 3.8 $mgO_3\,g^{-1}$ MLSS which showed that ozone could disrupt the cell walls and release the soluble microbial product.

Keywords: Ozonation; Activated sludge; Oxygen uptake rate; Protein; Polysaccharide

1. Introduction

Ozone is a powerful oxidant that can react with sludge molecules in two different ways: direct and indirect reaction mechanisms. In direct mechanism, the rate of reaction is lower and depends on the reactants structure. While in indirect mechanism hydroxyl radicals accelerate the oxidation processes [1].

Biological–chemical treatment method is one of the newest systems in the world. In this method, ozone with air are injected in the aeration tank where the biological treatment happens. Ozone injection to activated sludge system improves the performance of the system and adds specific advantages to the biological

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treatment system. Ozone has different effects on biological system such as: reduction sludge production [2]; powerful disinfection [3]; breaking slowly and non-biodegradable substances [4–7]; breaking the poisonous substances [8]; increasing the activity of microbial cells [8]; colour and smell elimination: [9]; reducing bulking problem; avoiding foaming problem [10]; mitigate fouling [11–14]; turbidity control. Ozone eliminates turbidity by making the suspended solid transient and neutralizing the charge of colloidal particles [7]; In addition, ozone injection can decrease the content of As and Cd and increase the metals such as Cr, Cu, Hg, Ni and Pb [15]. Moreover, ozone does not have any effect on Ca and Mg [16].

Ozone is a strong chemical oxidant that destroys the cell walls of microorganisms, which leads to the release of cytoplasm, as well as oxidation of many recalcitrant organic compounds. Sludge ozonation processes include sludge disintegration, solubilization and mineralization (oxidation of organic substances to CO_2). Solubilization efficiency depended on activated sludge characteristic and operational condition such as temperature. When the ozone concentration was 0.25–1.2 $gO_3\,g^{-1}$ MLSS the results showed that 30–60% of sludge were dissolved [17,18]. Economical estimates have suggested that the operational cost of the whole process of combining activated sludge and sludge ozonation was lower than that of the conventional activated sludge process when the costs of sludge dewatering and disposal were considered. Using a simple economic analysis showed that the ozonation process may be more economical than incineration for sludge treatment and disposal at small and medium-sized WWTP [16]. At ozone dosage of 50 $mgO_3\,g^{-1}$ DS, soluble chemical oxygen demand (SCOD), protein and polysaccharide increases to 1,356, 223 and 391 $mg\,L^{-1}$, respectively. Also, it was shown that the respirometric activity of sludge significantly decreased during 50 $mgO_3\,g^{-1}$ DS ozonation which represents that ozone destroys the cell walls [13].

Wu and Huang reported that ozonation can mitigate fouling with the dosage of 0.25 $mgO_3\,g^{-1}$ SS [11]. Moreover, ozonation significantly decreases the detrimental role of biopolymer on fouling. BPC after ozonation apparently lost their "gluing" capability to a great extent. As a result, it could decrease the solution viscosity. An ozone dosage of 0.03 mg/mg TOC on BPC could reduce the mean BPC size from 38 to 27 μm [14].

Since one of the drawbacks of ozonation is capital and operational costs, determining the optimum ozone concentration seems necessary. The results showed that ozone performance depends on the ozone injection time and ozone adsorption by sludge. As a result, it is needed to investigate the ozone effects with different concentration on sludge in order to use it in systems with high organic loading rate such as membrane bioreactor. The objective of experimental study was to determine ozone adsorption by activated sludge in order to evaluate the optimum ozone concentration in low volume to decrease the soluble microbial product (SMP).

2. Materials and methods

2.1. Operational condition

Activated sludge was collected from the wastewater treatment plant of Petroleum Company. It was adapted by synthetic wastewater including glucose, ammonium phosphate and ammonium nitrate for one month. The mixed liquid suspended solid (MLSS) was 11–14 $g\,L^{-1}$. The experiments were carried out at ambient temperature and pH between 7 and 7.5.

2.2. Ozone adsorption by activated sludge system

An oxygen contactor (Green life's made in France, Arda Company) with a maximum producing capacity of 5 $L\,min^{-1}$ was used to generate ozone and the ozone outlet was passed through two bottles which were filled with 2% KI solution. The amount of ozone leaving the ozone contactor was measured by iodometric method. In order to get more practical results the oxygen flow rate was set at 4 $L\,min^{-1}$. After ozonation, 10 mL sulphuric acid 2 N was added to the KI solution. After that the solution was titrated by tiosulphate sodium 0.05 N since the solution became yellow. Then, one or two mL Gliadin was added and the solution was titrated with tiosulphate sodium 0.05 N again since the blue colour disappeared. Finally, according to the amount of tiosulphate sodium ozone concentration was calculated with Eq. (1) [19].

$$\frac{mgO_3}{min} = \frac{(A + B) \times 24 \times N}{T} \tag{1}$$

where

- A — tiosulphate sodium which was used for the first bottle (mL)
- B — tiosulphate sodium which was used for the second bottle (mL)
- T — ozonation time (min)
- N — tiosulphate sodium normality

There were two bottles of KI solution after the activated sludge reactor for determining ozone consumption. The amount of ozone which was not adsorbed by sludge was neutralized in the KI solution. Ozone adsorbed in sludge was calculated based on the Eq. (2).

$$\text{Ozone concentration in sludge} = \frac{\text{ozone in} - \text{ozone out}}{\text{MLSS}} \quad (2)$$

where

ozone in — ozone left the generator
ozone out — ozone which was neutralized in KI solution
MLSS — mixed liquid suspended solid

2.3. Sludge characteristic

In this study, MLSS, MLVSS, SCOD, protein, polysaccharide, humic acid and pH were measured based on the standard method after ozonation [19]. Increasing SCOD showed that sludge disintegrated and entered the solution phase [5,16]. Protein, polysaccharide and humic acid showed the SMP which can be increased because of the disintegration in the solution. As a result it can increase the SCOD [16]. Protein and humic acid were determined based on the Frolund method while the polysaccharide was determined based on the Anthrone method [20].

3. Results and discussion

3.1. Ozone adsorption by sludge

Fig. 1 shows the amount of ozone adsorption vs. ozonation time in the activated sludge system with the MLSS = 11–14 g L^{-1} and SCOD = 600–3,500 mg L^{-1}. It was found that all of the injected ozone did not adsorb in sludge which is in accordance with the observations of Sui et al. [21]. With increasing the ozonation time (up to 40 s), ozone adsorption increased. After reaching the maximum value it decreased during the time. Based on the results the maximum amount of ozone which is adsorbed by sludge can be calculated. Producing ozone for sludge treatment is costly and is the major limitation to its use in full-scale plants. Optimization of sludge ozonation system must be one of the main scales in decreasing the cost of treatment system with ozonation [16].

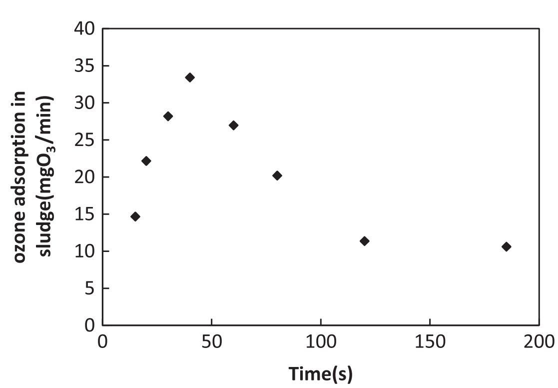

Fig. 1. Ozone adsorption in sludge vs. time.

Fig. 2 shows the ozone concentration in $mgO_3\,g^{-1}$ MLSS and MLSS in different ozonation times. The remarkable point is that ozone concentration increased until 60 s and after that until 120 it decreased slightly and finally it increased again. Based on the data (two points which are highlighted in the figure) it can be reached to the same ozone concentration (4 $mgO_3\,g^{-1}$ MLSS) for two different activated sludge systems with the same MLSS and different ozonation times (40 and 120 s). The results illustrate that only increasing the ozonation time cannot increase the ozone concentration in the system and ozone concentration should be determined in each system. Kinetic of ozone reaction in water and wastewater was given by Chik–Watson. Based on their law, the relation between ozone and reactant concentration is logarithmic; therefore, during the time by increasing ozone concentration the reactant concentration decreased then it became constant [22,23]. As a result it showed that ozone concentration which was absorbed by the reactant at first increased then it remained constant.

3.2. Mixed liquid suspended solid and mixed liquid volatile suspended solid/mixed liquid suspended solid

Fig. 3 shows the MLSS and MLVSS/MLSS changes during the different ozone injection concentrations. MLSS did not change during the ozone

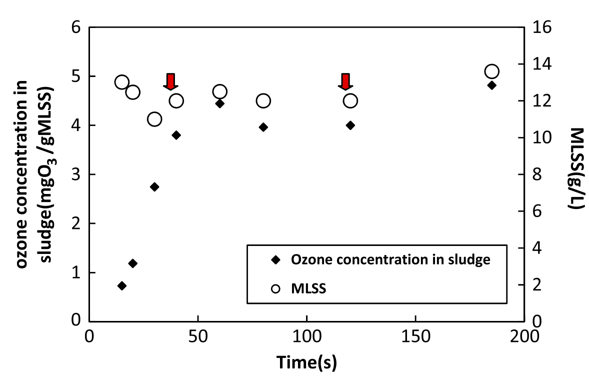

Fig. 2. Ozone concentration in sludge and MLSS vs. ozonation time.

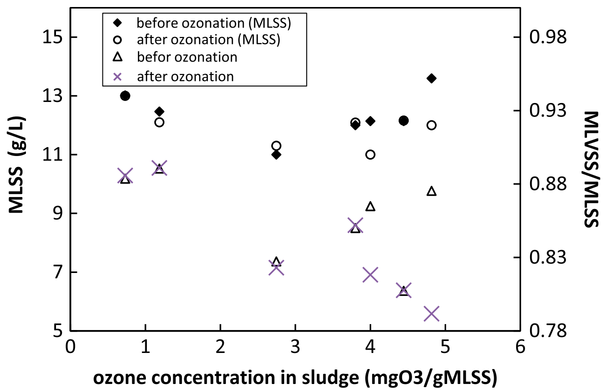

Fig. 3. MLSS vs. different ozone concentration.

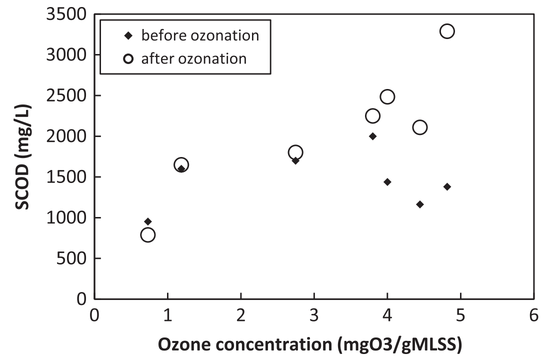

Fig. 4. SCOD vs. different ozone concentration.

injection until 3.8 $mgO_3\,g^{-1}$ MLSS and after that they decreased to 4 and 4.81 $mgO_3\,g^{-1}$ MLSS. The outstanding point is that in the 4.44 $mgO_3\,g^{-1}$ MLSS there was no decrease in MLSS concentration. This issue was caused by the shorter time of ozone contact with the microorganisms. The MLSS reduction is due to the fact that ozone destroyed the cell walls and produced the soluble product. This result is in accordance with the Wu and Huang study [13]. They reported that MLSS did not change with ozone concentration 0.25–0.7 $mgO_3\,g^{-1}$ SS [13].

Based on Fig. 3 MLVSS/MLSS in two ozone concentrations of 4 and 4.81, $mgO_3\,g^{-1}$ MLSS is lesser than before ozonation which is caused by the accumulation of inorganic suspended solid and oxidation of organic substances of cells.

3.3. Chemical oxygen demand

3.3.1. Soluble chemical oxygen demand

Fig. 4 displays the SCOD in different ozone concentrations. Results showed that in most of ozone doses injection, the SCOD increased after ozonation. In addition, it can be seen that in the 0.73 $mgO_3\,g^{-1}$ MLSS, SCOD decreased which is due to the fact that ozone destroys the SMP and oxidizes them in low concentration [3]. As shown in Fig. 4, except two ozone concentrations of 1.18 and 2.7 $mgO_3\,g^{-1}$ MLSS which SCOD did not change before and after ozonation, SCOD increased after ozonation since ozone disintegrated sludge microorganism. These results confirmed the Zhang et al. studies [15].

Huang and Wu assessed that 0.25 $mgO_3\,g^{-1}$ SS ozone injection did not have an effect on COD concentration [11]. This showed that most of the microorganism did not lose their activities during ozone injection.

3.3.2. COD in supernatant (COD supernatant)

Based on the data showed in Fig. 5, ozone injection in low ozone concentration (0.73–3.8 $mgO_3\,g^{-1}$ MLSS) increased the COD supernatant which was caused due to the fact that ozone disintegrated the sludge molecule and produced a solution with a higher turbidity [24]. Ozone decreased the extracellular polymeric substances (EPS) and broke down the bulks in low ozone concentration, therefore; it decreased the sedimentation rate [25]. Based on the data in Fig. 5, ozone injection in higher ozone concentration (0.73–3.8 $mgO_3\,g^{-1}$ MLSS) increased the COD supernatant which was caused due to the fact that soluble protein and polysaccharide increased. COD supernatant measurement could be an important operational parameter in the conventional activated sludge systems. The data showed that ozonation decreased the COD reduction efficiency in the conventional activated sludge systems.

3.4. Soluble microbial product

Sludge molecules, organic substances in supernatant and SMP had an effect on membrane fouling. Since the sludge molecules were bigger than membrane pore

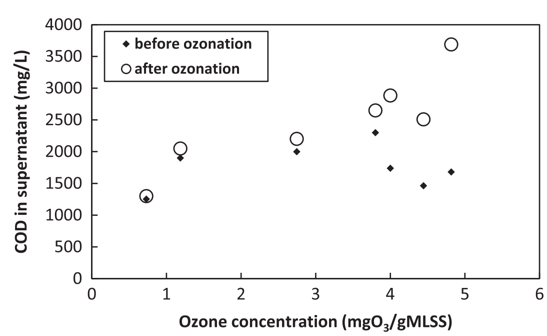

Fig. 5. COD of supernatant vs. ozone concentration.

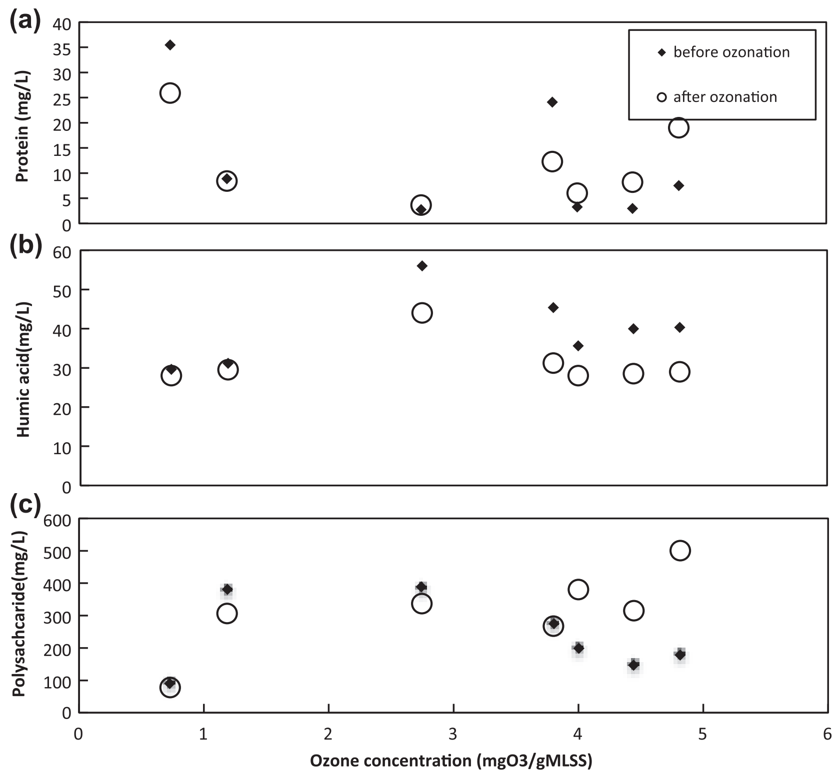

Fig. 6. Protein (a), humic acid (b) and polysaccharide (c) concentration vs. ozone concentration.

size; therefore, the main factor of fouling is the smaller particles such as protein, polysaccharide and humic acid which are the main components of SMP [26].

3.4.1. Protein, polysaccharide and humic acid

Fig. 6 shows the protein, polysaccharide and humic acid concentrations vs. different ozone doses. Based on the data in Fig. 6(a), protein content decreased with ozone injection until 3.8 $mgO_3\,g^{-1}$ MLSS which was due to the fact that ozone affected on protein, broke and changed them to the easily biodegradable product. It was shown that when the protein concentration is low in the solution, the effect of ozone on the protein concentration was neglectable. When the ozone concentration was higher than 3.8 $mgO_3\,g^{-1}$ MLSS, protein concentration increased in the system which was due to the breaking of microorganism and releasing the intercellular substances. Based on Fig. 6(b), it was shown that a reduction in humic acid concentration was more in higher ozone concentration. Totally it was observed that a reduction in the amount of humic acid happened due to the breakdown of them to lower molecular weight compounds. This result is in accordance with the Nguyen and Roddick [12].

Based on the data in Fig. 6(c), polysaccharide decreased after ozonation until the ozone injection is lower than 3.8 $mgO_3\,g^{-1}$ MLSS. When the ozone doses were higher than 3.8 $mgO_3\,g^{-1}$ MLSS, polysaccharide concentration increased after ozonation. It was observed that polysaccharide increase was more than protein which was due to the fact that at first ozone affect and broke the cell walls of microorganisms which has polysaccharide substances.

Huang and Wu observed that the EPS decreased when the ozone concentration was 0.25–0.75 $mgO_3\,g^{-1}$ SS, which showed that low ozone concentration could decrease the EPS content. Also they had demonstrated that when the ozone concentration was more than 8 $mgO_3\,g^{-1}$ SS, ozonation increased the EPS content which caused less filterability. They concluded that reduction of supernatant organic concentration, enlargement of flocs size and decrease of viscosity are the main reasons for the improvement of the mixed liquor's membrane filterability by ozonation [11].

4. Conclusions

Ozonation could be an efficient process in treatment systems based on choosing the optimum ozone concentration. It could be helpful in decreasing the sludge production and some SMPs such as protein, polysaccharide and humic acid. The main conclusions are as follows:

- With increasing the ozonation time (up to 40 s), ozone adsorption (mgO_3) by activated sludge increased. After reaching the maximum value it decreased during the time. Based on the result, optimum ozone concentration and the amount of ozone adsorbed by sludge should be calculated. In this study, the maximum ozone adsorption was in 40 s ozonation in the operational condition of MLSS = 11–14 g L^{-1} and SCOD = 600–3,500 mg L^{-1}.
- Ozonation in low concentration (less than 3.8 $mgO_3\,g^{-1}$ MLSS) did not have an effect on MLSS. While in higher concentration the solid concentration decreased. The MLVSS/MLSS ratio decreased since ozone destroyed the cells and entered all cellular materials to the soluble phase.
- Ozonation in low concentration (less than 3.8 $mgO_3\,g^{-1}$ MLSS) decreased SCOD while in high concentration (more than 3.8 $mgO_3\,g^{-1}$ MLSS) it increased SCOD.
- Proteins in the solution decreased when the ozone concentration is less than 3.8 $mgO_3\,g^{-1}$ MLSS, due to the fact that ozone broke up the proteins and converted them to the easily biodegradable product. While in higher ozone concentration (more than 3.8 $mgO_3\,g^{-1}$ MLSS) protein increased in the solution which is due to breaking up the microorganism and releasing the intercellular substances such as protein.
- Humic acid decreased after ozonation since ozone broke up the large HS to lower MW compounds.
- Polysaccharide decreased in the system when the ozone concentration was less than 3.8 mgO_3 g^{-1} MLSS and increased when the ozone concentration was more than 3.8 $mgO_3\,g^{-1}$ MLSS.

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