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Photocatalytic oxidation of waste activated sludge using a backlight photocatalytic reactor

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ABSTRACT

This study investigated the photocatalytic oxidation of waste activated sludge (WAS) in a backlight photocatalytic reactor. In this reactor, TiO_2 nanoparticles were fixed on a Plexiglas sheet. Waste activated sludge flowed from the coated section, and a UV lamp was located on the other side of the sheet. The effect of the TiO_2 nanoparticles' concentration (40, 60, 70, and 80 g/m^2) and WAS dilution (0, 2, 3, and 6 times dilution) was investigated on waste activated sludge photocatalytic oxidation. Chemical oxygen demand (COD) removal efficiency, volatile suspended solids (VSS) removal efficiency, soluble chemical oxygen demand changes, and soluble polysaccharide changes were measured after 200 min of WAS photocatalytic oxidation. The study of waste activated sludge dilution showed that the high waste activated sludge concentration (6,450 mg/L) caused no problem in COD and VSS removal. It was also revealed that the increased TiO_2 concentration elevated the WAS oxidation efficiency. The highest COD and VSS removal efficiencies were 37% and 38%, respectively, which were obtained in waste activated sludge without dilution and TiO_2 concentration equal to 80 g/m^2. Changes in soluble polysaccharide and COD showed that waste activated sludge photocatalytic oxidation in this reactor might lead to WAS solubilization. Also, an increase in waste activated sludge dilution and a decrease in TiO_2 concentration increased waste activated sludge solubilization.

Keywords: Photocatalytic oxidation; Hydroxyl radical; Photocatalytic reactor; Waste activated sludge; Sludge management

1. Introduction

The activated sludge process is used in wastewater treatment due to its high efficiency and ease of use. Waste activated sludge (WAS) is the by-product of wastewater treatment using the activated sludge process [1]. Waste activated sludge is a complex substrate that contains a complex structure and different types of microorganisms. Some efforts have been made to improve the performance of activated sludge but waste activated sludge production is part of the process and cannot be eliminated [2]. Since waste activated sludge consists of highly putrescible organic materials, it should be treated before evacuation to the environment. The waste activated sludge treatment and disposal cost is about 50% of the total operating costs of a wastewater treatment plant [3]. One step in WAS treatment is to stabilize its organic materials. Anaerobic digestion is the most widely used method in waste activated sludge stabilization. The problem here is that waste activated sludge contains hardly biodegradable organic materials and waste activated sludge anaerobic digestion might last up to 25 d. Besides, anaerobic digestion cannot always be used for WAS stabilization. In cases that the concentrations of sulfate, ammonium, and heavy metals are high in waste activated sludge, anaerobic digestion is not possible [4].

Different methods are used to remove organic contaminants. These methods can be classified into three categories: physical [5], chemical [6], and biological [7,8]. Ultrafiltration

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[5], nanofiltration [9], and reverse osmosis [10] are some of the physical methods used to treat organic contaminants. The main problem of these methods is membrane fouling [9,11]. Hence these methods are primarily used for effluent remediation [11]. Advanced oxidation processes (AOPs) are among the chemical methods used to treat organic contaminants [12]. These processes have high usability when standard biological methods have not good efficiency in removing organic contaminants. Heterogeneous photocatalytic process (HPO) is an AOP with the proven potential in eliminating organic contaminants, even hardly biodegradable [13]. In HPO, removing contaminants begins by absorbing ultraviolet (UV) radiation by a semiconductor catalyst [14]. TiO_2 is a semiconductor catalyst that has widely been used in HPO due to its characteristics [1]. Compared to anaerobic digestion, HPO operation is not highly complex. Photocatalytic oxidation is done using TiO_2 at a temperature below 80°C [13]. However, it is crucial to control the temperature condition of an anaerobic digester as one of the complexities in its operation process. Methanogenesis is another problem in the operation process of anaerobic digestion because it acts in the limited pH range of 6.5–7.2 [15], while photocatalytic oxidation occurs at every pH [13].

Materials science and its application are one of the main branches of research [16,17]. Research has shown that reducing the size of semiconductor materials improves their photocatalytic activity [18]. Therefore, nanosized TiO_2 is used to treat organic contaminants. In addition, it is possible to stabilize nanomaterials on different surfaces [19]. Therefore, due to the location of TiO_2 nanoparticles, reactors with different configurations have been created, including a baffled photocatalytic reactor [20], a polyethylene terephthalate (PET) flow reactor [14], a spinning disc photocatalytic reactor [21], a submerged membrane photocatalytic reactor [22], and a UV annular reactor [6]. Both UV radiation and organic contaminants reach the TiO_2 surface from one direction in these reactors.

In a study to treat turbid wastewater containing phenol, Khaksar et al. [23] developed a photocatalytic reactor in which UV radiation reached from one side and the wastewater from the other side to the TiO_2 surface. Their research showed that the turbidity of the wastewater had no adverse effect on the phenol removal efficiency. They used kaolinite to induce turbidity in the wastewater, and their purpose was to treat the phenol in the soluble phase. While almost all organic materials in WAS are enclosed in biological flocs, these flocs are in the solid phase [3]. There are studies about waste activated sludge photocatalytic oxidation [1,3,24–26], in which both UV radiation and waste activated sludge reach the TiO_2 surface on the same side. Waste activated sludge solids either prevent reaching UV radiation to the TiO_2 surface or reduce the rate of received radiation on the TiO_2 surface.

Nevertheless, UV radiation must reach the TiO_2 surface for the photocatalytic reaction [13]. In conventional reactors, it is not probable to expect WAS dilution to provide the possibility of receiving higher UV radiation on the TiO_2 surface [26]. Of course, dilution cannot be the desired solution since waste activated sludge is in the solution and absorbs UV radiation. Besides, even the cleanest water absorbs some UV radiation wavelengths suitable for photocatalytic reactions [27]. Since waste activated sludge is both the target of treatment and the absorber of UV radiation, the better solution is to separate the receiving side of UV radiation and WAS in the photocatalytic reactor. With this change, waste activated sludge solids and UV absorber impurities do not interfere with receiving UV radiation in the reactor. Therefore, WAS photocatalytic treatment in this type of reactor needs further studies.

In a backlight photocatalytic reactor, UV radiation and contaminant reach the TiO_2 surface from different sides, and the contaminant cannot intervene with the UV absorbance of TiO_2. This study aimed to examine the photocatalytic treatment of WAS in a backlight photocatalytic reactor. For this purpose, the effect of TiO_2 concentration and waste activated sludge dilution was investigated on the chemical oxygen demand (COD) and volatile suspended solids (VSS) removal efficiency and soluble polysaccharide and soluble chemical oxygen demand (SCOD) concentration.

2. Materials and methods

2.1. Materials

The photocatalyst used in this study was TiO_2 nanoparticles from Tecnan Company, (Spain). The mean diameter of the nanoparticles was 10–15 nm, and the crystal phase of them was 85% anatase and 15% rutile [23]. A NARVA Blacklight Blue lamp with 160 W electrical power was used as a UV-A radiation source, with an emission spectrum range of 350–400 nm and a peak of 365 nm. ARAKS 577 concrete adhesive was used to fix the TiO_2 nanoparticles. Other chemicals were of analytical grade procured from Merck Company, (Germany).

2.2. WAS sample characteristics

The samples were taken from the second phase of a wastewater treatment plant, north of Isfahan, with a nominal capacity of 800,000 people. The activated sludge process in this phase was absorption/bio-oxidation (A/B). The samples were taken from the return line of the sludge thickener related to the B aeration pond. The samples were transferred to the laboratory in less than 15 min. WAS sample characteristics are shown in Table 1.

Table 1
Characteristics of the sample taken from the secondary sedimentation return line

Factor*	Average value
Chemical oxygen demand (mg/L)	7,150
Soluble chemical oxygen demand (mg/L)	123.2
pH	7.1
Total suspended solids (mg/L)	6,450
Volatile suspended solids (mg/L)	4,950
Sludge volume index (mL/g)	60
Electrical conductivity (μS/cm)	980
Soluble polysaccharide (mg/L)	10

*WAS contained approximately 7,150 mg/L of COD; 123.2 mg/L of SCOD; 6,450 mg/L of TSS; 4,950 mg/L of VSS; 60 mL/g of SVI; 980 μS/cm of EC; 10 mg/L of soluble polysaccharide; pH 7.1.

2.3. Fixing method of TiO_2 nanoparticles

Photocatalyst particles should be coated on a transparent surface with suitable transmittance for UV radiation to provide the possibility to pass UV light in the backlight configuration. In this configuration, one side of the transparent surface is coated with TiO_2 nanoparticles, and the other side is exposed to the UV radiation source. A Plexiglas sheet is transparent, and it has suitable transmittance for UV-A radiation, but radiation with a wavelength shorter than 320 nm leads to photodegradation of the Plexiglas sheet [23]. The wavelength of the UV lamp was in the safe range for the Plexiglas sheet used in the study and thus the sheet was used as a transparent surface. In this configuration, nanoparticles should be fixed on the Plexiglas sheet such that it does not interfere with UV radiation transmittance. One method to fix nanoparticles is epoxy glue [28]. This method used epoxy glue to stick the TiO_2 nanoparticles on the surface. Plexiglas had good adhesion with epoxy glue and had a rigid structure that supported fixed nanoparticles in the backlight configuration [23]. There was also good adhesion between the TiO_2 nanoparticles and epoxy glue [28]. Hence a layer of epoxy glue was placed on the Plexiglas surface, and then the TiO_2 nanoparticles were fixed on it. The UV-A test (UVA-365 Lutron, Taiwan) showed that transparent epoxy glue and the Plexiglas sheet reduced UV-A transmittance by as much as 16%. Therefore, coating the TiO_2 nanoparticles with epoxy glue was suitable for this configuration.

TiO_2 nanoparticles were coated on the Plexiglas surface using the method proposed by Delnavaz et al. [28]. In this method, 300 mL of 30% epoxy glue was poured onto the Plexiglas surface. Then, it was placed at ambient temperature for 2 h to form a semi-dried surface of epoxy glue. The required amount of TiO_2 nanoparticles was added to 150 mL deionized water and dispersed well using an ultrasonic bath for 5 min. Next, TiO_2 solution was poured on the semi-dried surface of epoxy glue and left for 24 h at ambient temperature. Finally, the surface was rinsed with water to eliminate extra nanoparticles. Fig. 1 shows the scanning electron microscopy (SEM) image of Plexiglas coated with the TiO_2 nanoparticles.

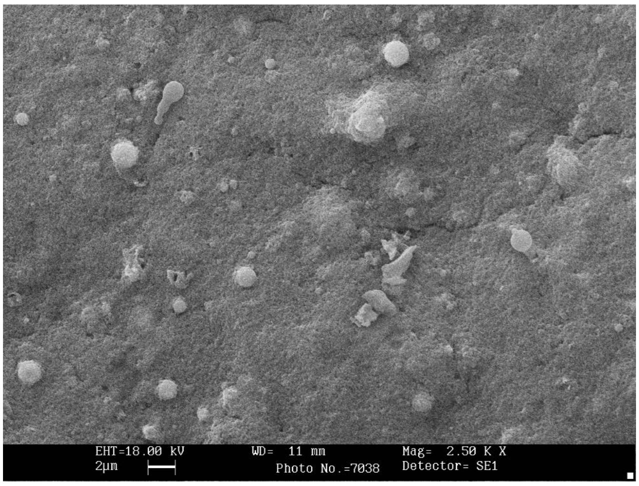

Fig. 1. SEM image of the TiO_2 nanoparticles coated on the Plexiglas sheet surface.

2.4. Backlight photocatalytic reactor

The backlight reactor consisted of a Plexiglas sheet coated with the TiO_2 nanoparticles, a WAS tank, a submerged pump, a UV-A lamp, a fan, and a four-legged metal frame. The coated sheet had dimensions of 420 mm × 250 mm × 2 mm and was placed on the four-legged metal frame without any slope. Four Plexiglas walls were placed on the perimeter of the coated sheet. The height was 4 cm in three of the walls and 2 cm in one of them. As a result, the created basin with a height of 2 cm was filled with 1.6 L waste activated sludge, and the wall with the height of 2 cm acted as the overflow. WAS was pumped from the tank onto the sheet surface using a submerged pump. The waste activated sludge tank was placed near the overflow and the four-legged metal frame, and extra waste activated sludge flowed into it. Total waste activated sludge in circulation was 6 L and was treated for 200 min. Pouring waste activated sludge from the overflow to the tank-mixed waste activated sludge with air and increased dissolved oxygen concentration. Liu et al. [26] showed that mixing WAS and air in a waste activated sludge tank was enough to provide the required oxygen for photocatalytic reaction. Besides, increasing the pumping rate increased the mix of waste activated sludge and air, thereby increasing waste activated sludge photocatalytic oxidation.

For this reason, WAS and the air was mixed in the waste activated sludge tank to provide the required oxygen. Waste activated sludge was pumped into the reactor using the submerged pump at a 20 L/min rate. Increasing the pump flow rate poured out waste activated sludge from the tank and was not possible. A UV-A lamp was placed at an 8 cm distance under the symmetry center of the coated sheet. A 25 W fan was placed near the lamp and conditioned the heat produced by it. Fig. 2 shows the configuration of the backlight photocatalytic reactor.

2.5. Design of experiments

The concentrations of the photocatalyst and WAS dilution are the two most effective variables of waste activated sludge photocatalytic oxidation [26]. This study examined the effect of these two parameters on waste activated sludge photocatalytic oxidation with a full-factorial experiment. The experiments were replicated three times, and the mean results were reported. The TiO_2 concentration values were selected according to Khaksar et al.'s study [23]. They recommended increasing the TiO_2 concentration up to 80 g/m^2. The dilution values were selected according to Liu et al.'s study [26]. They recommended increasing WAS dilution to 7.5 times. Table 2 shows the values used for these two parameters.

2.6. Analysis methods

Several tests were conducted on the samples to determine WAS solubilization and oxidation. The liquid and solid phases were separated using a membrane filter (0.45 μm

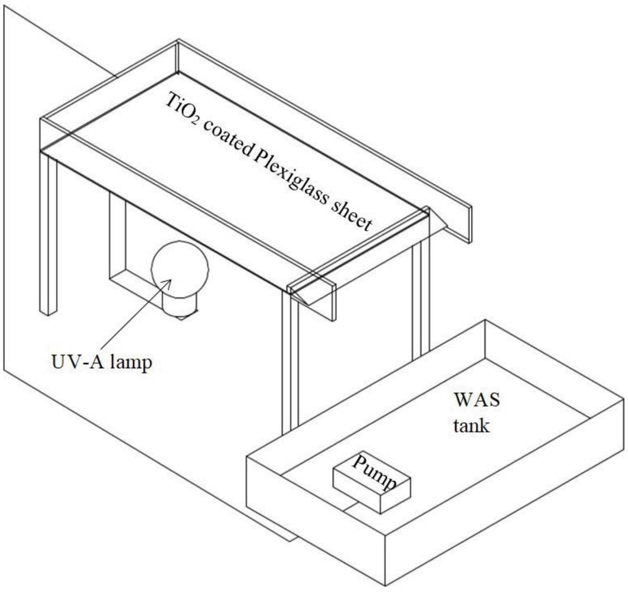

Fig. 2. Configuration of the backlight photocatalytic reactor.

Table 2
WAS photocatalytic oxidation parameters

Parameter	Values
TiO_2 concentration	40, 60, 70, and 80 g/m^2
WAS dilution	No dilution, two times dilution, three times dilution, six times dilution

cellulose acetate) to measure the amount of the waste activated sludge solubilization [29]. The term "solubilization" indicates COD or solids transmission from particulate waste activated sludge to soluble waste activated sludge [30].

The COD test indicates the total efficiency of WAS disintegration [3]. In this study, the COD test on the solution that remained from filtration was called "soluble chemical oxygen demand". Tests related to COD and SCOD were conducted based on Standard Methods 5220-D [31]. SCOD is expressed as the difference between the SCOD of the sample after photocatalytic oxidation and that of the control sample. The COD removal efficiency was calculated based on the difference between the COD of the control sample (COD_0) and COD after photocatalytic oxidation divided into COD_0:

$$\text{COD removal efficiency}\left(\%\right) = \frac{\left(\text{COD}_0 - \text{COD}\right)}{\left(\text{COD}_0\right)} \times 100\% \quad (1)$$

The Dubois method was used to measure the polysaccharide concentration in the solution [32]. 1 mL of the sample (after filtration) was added to 1 mL of 5% phenol solution and 5 mL of 95% sulfuric acid. After 10 min, the sample was shaken and left at ambient temperature for 30 min. Then, the sample's absorption was measured at a 490 nm wavelength using a spectrophotometer (DR/2500, HACH, USA). Glucose was used as the standard material. Soluble polysaccharide is expressed as the difference between the concentration before and after photocatalytic oxidation.

VSS changes are more important than changes in total solids while concerning waste activated sludge disintegration [26]. The VSS test was performed based on Standard Methods 2540-E (APHA 2005). VSS removal efficiency was calculated based on the difference between the VSS of the control sample (VSS_0) and sample VSS after photocatalytic oxidation divided into VSS_0:

$$\text{VSS removal efficiency}\left(\%\right) = \frac{\left(\text{VSS}_0 - \text{VSS}\right)}{\left(\text{VSS}_0\right)} \times 100\% \quad (2)$$

3. Results and discussion

3.1. COD removal efficiency

WAS photocatalytic oxidation has four steps. The first step is to destroy the structure of biological floc and floc solubilization; the second step is to oxidize solubilized floc; the third step is to destroy the cellular wall and release intracellular material into the solution; the fourth step is to oxidize released intracellular substances. The oxidation strength of the process determined how much waste activated sludge was oxidized. The results showed that an increase in WAS dilution reduced the oxidation strength. As shown in Fig. 3, the increase in waste activated sludge dilution led to a decrease in the COD removal efficiency. For example, in waste activated sludge photocatalytic oxidation without dilution and the TiO_2 concentration of 40 g/m^2, the COD removal efficiency was 12%. By increasing dilution to six times, the COD removal efficiency was reduced to 2.5%.

Manterola et al. [30] reported a similar behavior for oxidation with ozone. They reported that by increasing the waste activated sludge concentration in fixed ozone concentration, the waste activated sludge oxidation rate increased. They concluded that this occurred likely due to the high speed of oxidation with ozone. Déléris et al. [33] and Cesbron et al. [34] reported similar results in WAS oxidation with ozone. The hydroxyl radical produced in the sheet coated with TiO_2 nanoparticles is the main factor in eliminating organic contaminants in photocatalytic oxidation [13]. In the oxidation of organic contaminants, the hydroxyl radical reaction rate is 10^6 to 10^7 times higher than ozone [35], and its life span is very short [36]. Therefore, the waste activated sludge oxidation occurs near the coated surface. When waste activated sludge was diluted, there was less WAS near the coated surface, and the COD removal efficiency was reduced. Photo-Fenton is one of the AOPs. Tokumura et al. [37] reported a similar result in the study of waste activated sludge treatment using this process. They examined WAS oxidation in two configurations, one with higher oxidation strength and lower waste activated sludge concentration (3,000 mg/L) and the other with lower oxidation strength and higher waste activated sludge concentration (5,000 mg/L). The result showed that waste activated sludge disintegration in both configurations was almost equal. Ultrasonic is another AOP that can be used for WAS treatment. Wang et al.'s [38] experiments showed that waste activated sludge disintegration was doubled in the ultrasonic treatment of

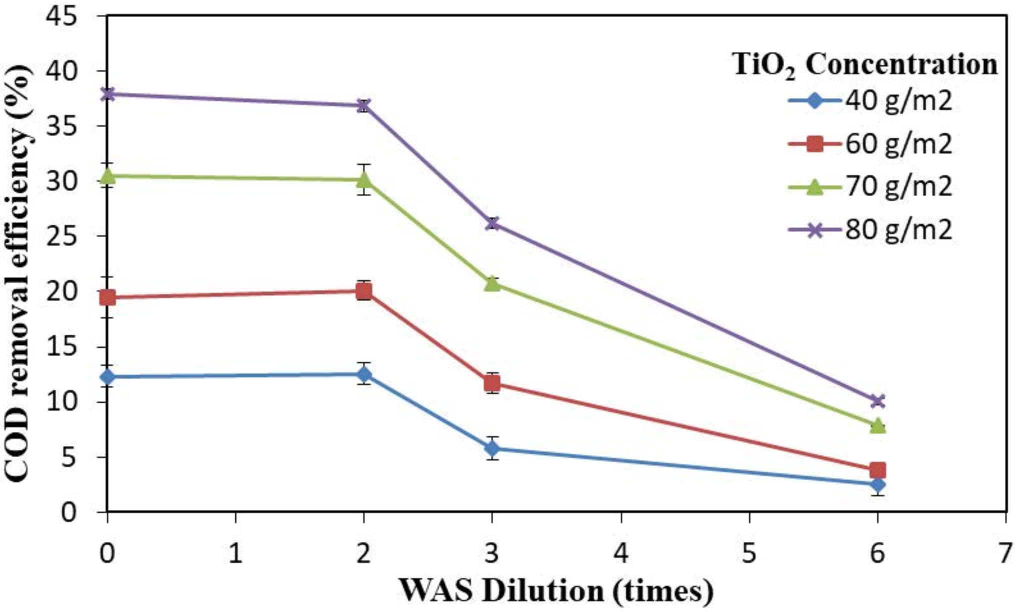

Fig. 3. Effect of WAS dilution and TiO_2 concentration on the COD removal efficiency of waste activated sludge after the 200 min photocatalytic treatment (error bars represent standard deviation among duplicate tests).

waste activated sludge at constant process conditions by increasing WAS concentration from 0.5% to 1%.

For TiO_2 concentrations of 40, 60, 70, and 80 g/m^2, the COD removal efficiency without dilution had a value below the one with two-time dilution. By reducing dilution from two times to no dilution, the density of WAS solids increased, and the contact between solids made the solids far from the coated surface. Therefore, by reducing dilution from two times to no dilution, the removal efficiency was changed to less than 1%.

However, different results were obtained in no backlight reactor. Liu et al. [26] studied WAS photocatalytic oxidation in a circulating bed photocatalytic reactor. They coated TiO_2 on zeolite balls with a 3.5 mm diameter. Zeolite balls submerged in waste activated sludge and UV-A radiated from the above reactor to the balls. They investigated the effect of waste activated sludge 0, 2.5, 5, 7.5, 10, and 15 times dilution on waste activated sludge photocatalytic oxidation. They reported that by increasing dilution, the waste activated sludge oxidation rate also increased. The difference between the results in these two studies is as follows. In conventional photocatalytic reactors, in which both UV and waste activated sludge reach the same side of the photocatalyst, diluting waste activated sludge reduces the organic matter concentration and reducing the turbidity, increases UV light transmittance. Since reaching UV radiation to the surface of the photocatalyst is necessary for the photocatalytic reaction, WAS dilution in these types of reactors causes a photocatalytic reaction to occur; therefore, in higher concentrations, no photocatalytic reaction occurs because UV radiation does not reach the photocatalyst surface. However, in the backlight reactor, due to changing the UV source position, changing waste activated sludge dilution will not change the amount of UV light received on the surface of the photocatalyst, and the photocatalytic reaction occurs regardless of WAS dilutions. In other words, in the backlight reactor, the active area was higher than conventional photocatalytic reactors since waste activated sludge solids never intervene in receiving UV radiation on the TiO_2 surface. Therefore, the backlight reactor has coped with the negative characteristic, that is, high WAS concentration. Another disadvantage of fixed bed reactors is that a part of the nanoparticles is wasted due to fixing on the surface [13]. However, in the backlight reactor, a part of nanoparticles coated on the surface by fixing is used for absorbing UV radiation.

Contrary to other configurations with fixed beds, this configuration used the nanoparticles better. The quality of the coating also affected the fixed bed photoreactors' performance [28]. Fig. 1 shows an SEM image of the Plexiglas sheet coated by the TiO_2 nanoparticles with 40 g/m^2 in the micrometer scale. As the image shows, the TiO_2 nanoparticles were uniformly distributed on the Plexiglas surface.

As shown in Fig. 3, by increasing TiO_2 concentration, the COD removal efficiency also increased. For example, in photocatalytic oxidation with the TiO_2 concentration of 40 g/m^2 and waste activated sludge without dilution, the COD removal efficiency was 12%, which increased to 37% by increasing TiO_2 to 80 g/m^2. This increase is because by increasing TiO_2 concentration, the rate of hydroxyl radical production also increased [13], and as a result, the COD removal efficiency increased. Khaksar et al. [23] concluded that the process efficiency would not significantly improve in the backlight reactor by increasing TiO_2 concentration above 80 g/m^2 because it was more than surface coating capacity. Therefore, TiO_2 concentration was studied up to 80 g/m^2. The error due to this measurement was less than 15%.

3.2. SCOD variations

As shown in Fig. 4, the SCOD difference had both negative and positive values. The positive values indicated that

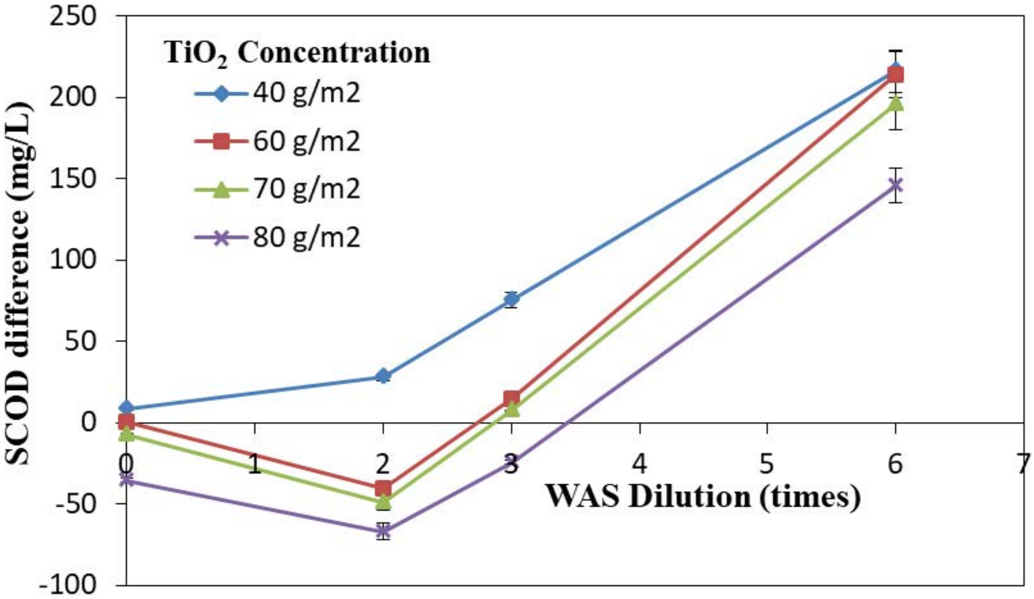

Fig. 4. Effect of WAS dilution and TiO_2 concentration on the SCOD difference of waste activated sludge after the 200 min photocatalytic treatment (error bars represent standard deviation among duplicate tests).

the SCOD value after photocatalytic oxidation was higher than the control sample and that WAS was solubilized. The negative values revealed that the SCOD value was lower than the control sample after photocatalytic oxidation. The error due to this measurement was less than 15%.

The formation of a biological floc that is later disposed from an aeration basin of activated sludge as WAS is as follows. The grains play the role of the core for the floc, attracting many microorganisms and forming tiny flocs. Macromolecules secreted from microorganisms, including polysaccharides, organic acids, nucleic acids, and lipids, convert this set to a three-dimensional loose set. These secreted macromolecules are called extracellular polymeric substances (EPS) [39]. During this process, a considerable amount of water is enclosed into the biological floc [40]. As mentioned in Section 3.1 (COD removal efficiency), WAS photocatalytic oxidation has four steps. In the first and third steps, organic matters in the biological floc and the intracellular material enter the solution and increase SCOD concentration in the solution. Then, a part of SCOD in the solution is oxidized and removed [3].

By decreasing the oxidation power of the system, less SCOD was removed and caused more solubilized WAS to remain after oxidation. By increasing dilution more than two times, the biological floc became more soluble and the SCOD difference was positive because the effective contact between hydroxyl radical and waste activated sludge was reduced and WAS oxidation decreased. For example, in waste activated sludge photocatalytic oxidation with three times dilution and the TiO_2 concentration of 40 g/m^2, the SCOD difference was 75 mg/L. By increasing dilution to six times, the SCOD difference increased to 216 mg/L. In treating waste activated sludge with six times dilution, the SCOD difference was positive in all the experiments. For TiO_2 concentrations of 60, 70, and 80 g/m^2, the value was more in the SCOD difference without dilution than the one with two times dilution. The reason is likely that the density of waste activated sludge solids increased and solids moved away from each other and the coated sheet. Therefore, WAS oxidation decreased, and waste activated sludge without dilution was solubilized more than two times dilution. Besides, reducing TiO_2 concentration increased waste activated sludge solubilization. In treating WAS with a TiO_2 concentration of 40 g/m^2, the SCOD difference was positive for all waste activated sludge dilutions. The reduction of TiO_2 concentration reduced the production of hydroxyl radicals in the solution as well. Therefore, decreasing TiO_2 concentration led to a decrease in waste activated sludge oxidation and produced more soluble waste activated sludge. The highest solubilization was obtained with a TiO_2 concentration of 40 g/m^2 and six times dilution up to 216 mg/L compared to the control sample. Manterola et al. [30] reported a similar phenomenon in waste activated sludge oxidation with ozone such that first waste activated sludge was solubilized and then by increasing the amount of ozone, waste activated sludge mineralization began. Tokumura et al. [37] reported a similar result in the study of waste activated sludge treatment using the photo-Fenton process.

3.3. Changes in soluble polysaccharide

Polysaccharide is a part of EPS and the structure of the biological floc [40]. Fig. 5 shows soluble polysaccharide differences due to photocatalytic oxidation. A positive difference indicated that the concentration of soluble polysaccharides after photocatalytic oxidation was higher than that of the control sample. Moreover, the negative difference showed that after photocatalytic oxidation, the amount of soluble polysaccharide was lower than that of the control sample. The error due to this measurement was less than 10%.

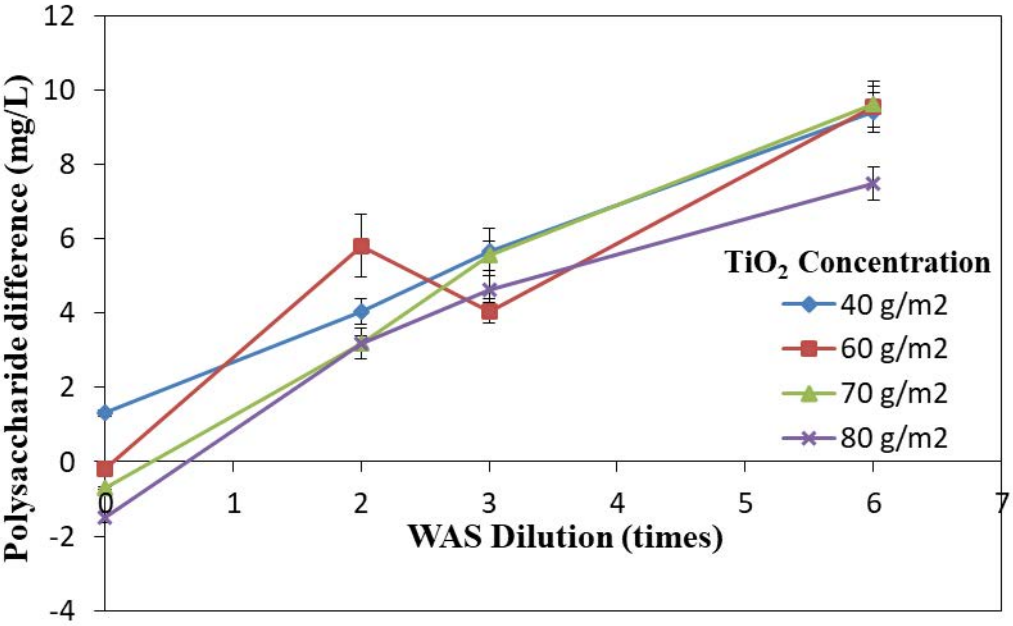

Fig. 5. Effect of WAS dilution and TiO_2 concentration on the soluble polysaccharide difference of waste activated sludge after the 200 min photocatalytic treatment (error bars represent standard deviation among duplicate tests).

When TiO_2 nanoparticles are excited by UV radiation with a wavelength shorter than 400 nm, they produce a pair of an electron (e^-) and a hole (h^+). The e^-/h^+ is transferred to the TiO_2 surface and participates in a chain of oxidation–reduction reactions. Hydroxyl radical is the result of water oxidation in h^+ and a chain of reactions related to e^-. Besides, the produced h^+ is also considered a contaminant oxidizer, but the contaminant should be adsorbed to play its role. The electrostatic forces between TiO_2 and the contaminant determine the adsorption rate. The surface charge of TiO_2 and the contaminant charge determine that the electrostatic forces have repulsive or attractive interactions or no interactions [13]. The surface charge of TiO_2 can be positive, negative, or neutral.

Regarding the point of zero charge (PZC), the pH of the solution determines the TiO_2 surface charge. PZC is a condition, in which the TiO_2 surface charge is zero or neutral. For all types of TiO_2, the PZC condition occurs in the pH range of 4.5 to 7. When the solution pH is more than the pH of PZC, the surface charge of TiO_2 is negative [13].

WAS photocatalytic oxidation begins with the contact of the biological floc and the TiO_2 photocatalyst surface. The charge of the biological floc is negative [40]. Since pH in all the experiments was 7.1, the TiO_2 surface charge was also negative. Therefore, the electrostatic forces between the biological floc and the TiO_2 surface were of repulsive type. As a result, oxidation with h^+ was not the starter of the biological floc oxidation, and oxidation with hydroxyl radical disintegrated the biological floc. Since EPS was the barrier between microorganisms and outer space in the biological floc structure [40], waste activated sludge photocatalytic oxidation began with the contact of EPS in the biological floc and hydroxyl radical. Then, the biological floc was disintegrated, and insoluble organic materials, including polysaccharides, were converted to soluble substances; therefore, the polysaccharide concentration increased in the solution. Besides, a part of the water enclosed in the biological floc entered the solution.

Polysaccharide is a natural polymer consisting of one or several types of monosaccharides. Monosaccharides are weak acids, and their acid dissociation constant (pKa) is slightly higher than 12. If the pH of the solution is higher than pKa, monosaccharides in the solution become anionic [41]. Since the pH of WAS was 7.1, almost all solubilized polysaccharides were not anionic. Therefore, there was no repulsion between polysaccharides and the TiO_2 surface.

Consequently, polysaccharide is oxidized by h^+ and hydroxyl radical, where h^+ is more active than hydroxyl radical [13], and this can increase the polysaccharide removal efficiency. For oxidation with h^+, polysaccharide must be closed to the coated surface. Mixing determines the presence of polysaccharide on the coated surface. Therefore, regarding the non-selective feature of photocatalytic oxidation [42], no organic material is preferred to others. Thus, the increased hydroxyl radical and h^+ production on the surface due to the increased photocatalyst concentration did not directly increase polysaccharide removal. As a result, the reduction of WAS dilution and the increase in the contact between hydroxyl radical and waste activated sludge had no direct effect on polysaccharide removal. The polysaccharide concentration, after photocatalytic oxidation, changed for waste activated sludge with two times, three times, and six times dilution for TiO_2 concentrations of 40, 60, 70, and 80 g/m^2 between 3 to 9 mg/L. This phenomenon is not observed in SCOD changes because polysaccharide and other soluble organic materials are a part of SCOD, and soluble organic materials immediately become oxidized or are exposed to the coated sheet and then oxidized.

3.4. VSS removal efficiency

As mentioned in Section 3.1, WAS photocatalytic oxidation has four steps. VSS removal indicated the destruction of the biological floc. Therefore, VSS was reduced in the first and third steps. Fig. 6 shows the VSS removal efficiency. To what step waste activated sludge is oxidized depends on waste activated sludge dilution, hydroxyl radical, surface roughness, and mixing. Since waste activated sludge consists of biological flocs and these flocs are in the solid phase, there is friction between biological flocs and the coated sheet. Since the photocatalytic reaction occurs in a fraction of a second [13], the friction can change the oxidation extent by increasing the retention time of the biological floc. The coated sheet was made by fixing the TiO_2 nanoparticles; thus, the nanoparticles created an unsmoothed surface in nano dimensions on the sheet.

Novotný et al. [43] investigated the friction coefficient of the surface coated with TiO_2 nanoparticles. The results showed that the coating increased the friction coefficient, and with an increase in TiO_2 concentration, the friction coefficient also increased. Therefore, by increasing TiO_2 concentration, the unsmooth parts of the surface and the friction between the surface and the biological floc also increased. Another factor that changes the physical contact of the biological floc and the coated sheet is WAS dilution. The density of biological flocs increases with decreasing waste activated sludge dilution, and the impact effect of flocs increases in transferring the flocs from the coated sheet.

In the photocatalytic oxidation of TiO_2 with 40 and 60 g/m^2 concentrations, the VSS removal efficiency with six times dilution was more than photocatalytic oxidation in other dilutions. By reducing dilution to three times and lower, the flocs' effect increased on transferring other flocs from the coated sheet and the VSS removal efficiency decreased. By decreasing dilution to two times caused by an increase in waste activated sludge concentration, the effective contact between the biological floc and hydroxyl radical increased, and as a result, the VSS removal efficiency was enhanced. For fixed TiO_2 concentrations at 70 and 80 g/m^2, the roughness of the coated surface increased and reduced the effect of the flocs' density on each other. In these conditions, the VSS removal efficiency was equal for waste activated sludge with six times and three times dilution. By reducing dilution to two times caused by the increase in WAS concentration, the contact between the biological floc and hydroxyl radical increased, thereby increasing VSS removal. For TiO_2 concentrations of 40, 60, 70, and 80 g/m^2, by reducing dilution from two times to no dilution, the removal efficiency changed to less than 3% because the flocs' density prevented them from approaching the coated sheet. The roughness effect of the coated surface and flocs' density on waste activated sludge disintegration occurs when waste activated sludge is solid. It is not effective in waste activated sludge photocatalytic oxidation after solubilization. The VSS removal efficiency was calculated using Eq. (2), and the error due to this measurement was less than 15%.

Using anaerobic digesters is the most common method to stabilize WAS in wastewater treatment plants around the world. One main goal of using an anaerobic digester is to reduce waste activated sludge quantity [4]. However, it is less efficient due to the floc structure because EPS and substances in the cellular wall of microorganisms reduce the anaerobic digestion efficiency [3]. For this reason, waste activated sludge anaerobic digestion was reduced by about 30% to 35% of VSS after 20–25 d [4]. However, organic materials underwent similar photocatalytic oxidation due to the non-selective characteristic of this type of oxidation [42]. In this study, the highest VSS removal efficiency was 38% after 200 min of waste activated sludge photocatalytic oxidation without dilution and the TiO_2 concentration of 80 g/m^2. Liu et al. [26] reported a similar result in the study of waste activated sludge treatment using a circulating bed photocatalytic reactor. They realized that photocatalytic oxidation could remove waste activated sludge volatile solids much faster than anaerobic digestion. The highest removal

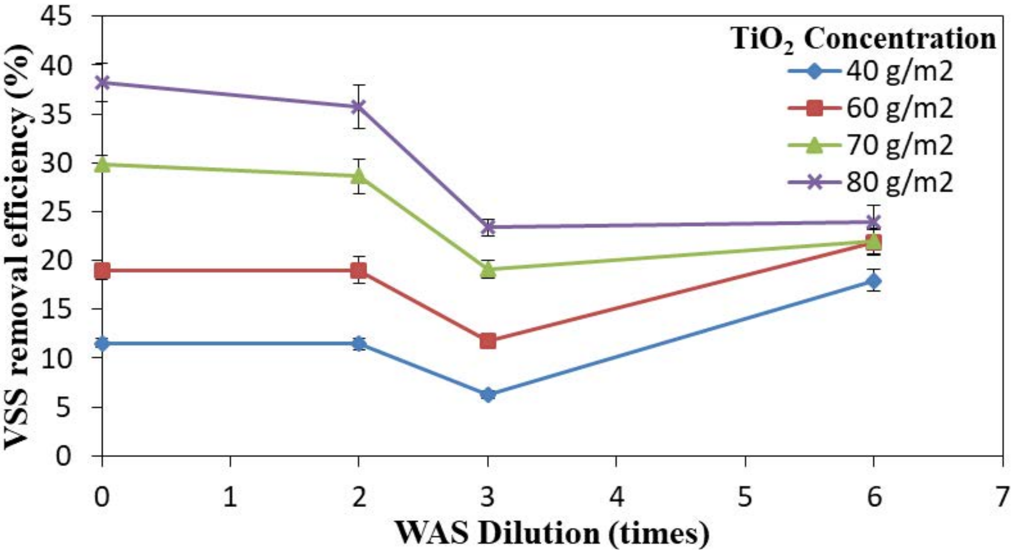

Fig. 6. Effect of WAS dilution and TiO_2 concentration on the VSS removal efficiency of waste activated sludge after the 200 min photocatalytic treatment (error bars represent standard deviation among duplicate tests).

Table 3
Analysis of variance for WAS photocatalytic oxidation

Response	Source of variation	DF	Sum of square	*F*	*p*
COD removal efficiency	Dilution	3	2,915.86	854.73	<0.001
	TiO$_2$ concentration	3	2,703.96	792.62	<0.001
	Dilution *TiO$_2$ concentration	9	351.51	34.35	<0.001
	Error	32	36.39		
	Total	47	6,007.71		
SCOD difference	Dilution	3	376,119	2,393.51	<0.001
	TiO$_2$ concentration	3	36,435	231.86	<0.001
	Dilution *TiO$_2$ concentration	9	7,611	16.14	<0.001
	Error	32	1,676		
	Total	47	421,841		
Soluble polysaccharide difference	Dilution	3	521.503	917.40	<0.001
	TiO$_2$ concentration	3	18.606	32.73	<0.001
	Dilution *TiO$_2$ concentration	9	22.490	13.19	<0.001
	Error	32	6.064		
	Total	47	568.664		
VSS removal efficiency	Dilution	3	661.91	141.75	<0.001
	TiO$_2$ concentration	3	2,349.35	503.13	<0.001
	Dilution *TiO$_2$ concentration	9	497.78	35.53	<0.001
	Error	32	49.81		
	Total	47	3,558.85		

efficiency, equal to 47%, was achieved after 8 h of waste activated sludge treatment with 7.5 times dilution.

3.5. Analysis of variance

Table 3 summarizes the results of variance analysis for WAS photocatalytic oxidation. Variance analysis was done at a 95% confidence level. This analysis confirmed that both TiO$_2$ concentration and waste activated sludge dilution were effective in the COD removal efficiency, VSS removal efficiency, soluble polysaccharide difference, and SCOD difference, and interacted with each other.

4. Conclusions

This study showed that the photocatalytic oxidation of WAS could be a suitable method to remove VSS in waste activated sludge. The study investigated the effect of waste activated sludge dilution and TiO$_2$ concentration on the photocatalytic treatment of WAS. The backlight photocatalytic reactor's performance was satisfactory in the treatment of waste activated sludge without dilution. The results showed that waste activated sludge solids were solubilized and removed due to photocatalytic oxidation. The COD and VSS removal efficiency increased with a decrease in waste activated sludge dilution and an increase in TiO$_2$ concentration. The highest VSS and COD removal efficiency was 38% and 37%, respectively, in waste activated sludge photocatalytic oxidation without dilution and the TiO$_2$ concentration of 80 g/m^2. This removal efficiency was obtained in 200 min, while waste activated sludge anaerobic digestion needs more time to achieve this efficiency.

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