Distribution of Detergent Waste in the Environment and the Removal by Using Photocatalytic Degradation and Coagulation Methods

Eko Sugiharto[1*], Adhitasari Suratman[2], Taufik Abdillah Natsir[3] and Endang Tri Wahyuni[4]

[1]*Chemistry Department, Faculty of Mathematic and Natural Sciences Gadjah Mada University, Yogyakarta, Indonesia.*

Authors' contributions

This work was carried out in collaboration between all authors. Author ES designed the study, performed the statistical analysis, and wrote the first draft of the manuscript, while author TAN performed the sampling and wrote the protocol, author AS corresponded the coagulation study, and author ETW corresponded the photodegradation study. Furthermore, all authors read and approved the final manuscript.

ABSTRACT

Aims: This study is aimed to determine the distribution of detergent contamination in the Code River and the ability to remove it from laundry wastewater samples by using photocatalytic degradation and coagulation methods.
Place and Duration of Study: The study was located at the Code River close to Gadjah Mada University, Yogyakarta, and the research was conducted for 6 months (June-November 2013).
Methodology: The water samples used in this study consist of waste water (produced from laundry activities) and river water (before and after the outlet of laundry waste disposal). Analysis of anionic surfactant and phosphate were carried out by UV/visible spectrophotometric methods using methylene blue and ammonium molybdate, respectively as complexing agents. The surfactant removal was studied using photocatalytic degradation and that of phosphate by coagulation methods. The photocatalytic reaction was carried out in batch technique by irradiating the artificial waste in the presence of TiO_2

Corresponding author: Email: ekosugiharto@ugm.ac.id;

powder as photocatalyst with UV lamp. The coagulation was conducted by batch technique using 3 types of coagulants, that are alum (Al^{3+}), ferroin (Fe^{3+}), and calcium (Ca^{2+}), in which the influence of reaction time was studied.

Results: The results indicate that the river water which is located at the points before and after the disposal point of the laundry waste water contain anionic surfactant and phosphate.The content of the anionic surfactant (198 mg/L) and phosphate (52 mg/L) in the laundry waste water (taken directly from the laundry process) are found to be much higher than the quality standard level (0.2 mg/L and 0.1 mg/L for surfactant and phosphate respectively). Therefore, it is clear that such waste water has to be treated before being disposed. The present study shows that the waste water treatment by photodegradation method catalyzed by TiO_2 can decrease the surfactant concentration effectively, and the effectiveness is controlled by TiO_2 dose and reaction time. The maximum removal of surfactant (90%) from 50 ml of the waste water can be obtained by using 30 mg of TiO_2 for 24 h of reaction time. By using coagulation process, the concentration of phosphate in the waste water can be decreased as much as 10-70%, depending on the type of coagulants. The most active coagulant is Fe^{3+} followed by Al^{3+} and Ca^{2+} due to their affinity in poly nuclear formation.

Conclusion: The water streams in the Code River are found to be contaminated by surfactant and phosphate in low to medium level. The removal of the surfactant in the laundry waste water was successfully carried out by photodegradation method catalyzed by TiO_2, while the phosphate concentration can be decreased by coagulation method.

1. INTRODUCTION

Detergent is intensively and widely used for domestic laundry and other cleaning purposes. The use of laundry detergent could produce waste water containing high concentrations of alkyl benzene sulphonate (ABS), and phosphate, which are known as the surface active agent (surfactant) and filler in most detergents, respectively. Since ABS is known as a hazardous chemical [1,2], and phosphate can promote eutrophication of plants, disposing the laundry waste water directly into the environment can pollute water supplies, remove oxygen from water supplies, promote growth of algae in water supplies and promote toxicity in plants and animals [1]. The increase in the number of laundry services, as found in Yogyakarta, consequently increases the volume of waste water, and furthermore causes the increase of chemical level in the environment. Since the chemicals found in waste water are known to cause hazardous effects, the detection of their presence and concentration level is important to be carried out in order to find out the distribution pattern in the environment. When the distribution of anionic surfactant and phosphate in the environment is known, a warning for people not to take or consume the water of a certain source can be announced. In addition, it is important to develop and apply a wastewater treatment process in order to to remove or at least decrease the release of ABS to the environment.

Several methods for decreasing dodecyl benzene sulfonate (DBS), a type of ABS, in detergents have been studied, including adsorption with furnace bottom ash [3], biodegradation involving microbes [4], and photolysis by UV light [5], as well as photocatalytic degradation using a combination of UV light and TiO_2 photocatalyst [6,7,8,9]. Among these methods, photocatalytic degradation has attracted much attention due to its

simplicity and effectiveness. However, the application of the method for real laundry waste water has not been explored yet. Accordingly, photocatalytic degradation with TiO_2 for DBS removal is examined.

Moreover, the removal of anionic phosphate has been carried out by the adsorption technique using modified zeolite [10]. Other phosphate removal methods from wastewater were also studied, such as using magnetic filtration by schwertmannite [11], using biosolids [12] and using oven-dried alum sludge [13]. Since phosphate can be suspended in water and make the water turbid or unclear, the removal should involve the use of coagulation methods [14]. In the present study, the use of alum, ferroin, and calcite as coagulants for phosphate removal from laundry waste water is studied.

2. MATERIALS AND METHODS

2.1 Chemicals and Instruments

Titanium dioxide, anatase (TiO_2, 79.866 g/mol), trisodium phosphate (Na_3PO_4, 163.94 g/mol), ammonium molybdate (($NH_4)_2MoO_4$, 196.02 g/mol), ascorbic acid ($C_6H_8O_6$, 176.12 g/mol), methylene blue (MB) ($C_{16}H_{18}N_3SCl$, 319.85 g/mol) and sodium dodecylbenzene sulfonate ($C_{12}H_{25}$-C_6H_4-SO_3 Na, 348.48 g/mol) (DBS), calcium chloride ($CaCl_2$, 110.98 g/mol), Iron (III) chloride ($FeCl_3$, 162.2 g/mol) and alum with Pro Analysis grade were purchased from E.Merck.

A closed reactor (60 x 40 x 120 cm) was used for the photoreaction processes, installed with a black light blue (BLB) UV lamp, 40 watt 220 volt with wavelength of 340-390 nm, A GBC Cintra 110 type UV/Visible spectrophotometer, and a Perkin-Elmer Atomic Absorption Spectrometer (AAS) were also used for analysis.

2.2 Procedure

2.2.1 Sample preparations

The laundry waste water samples were taken directly from the laundry outlet during the washing step/before the rinsing step. Whereas the river water samples were taken from the water surrounding the laundry outlet. These samples were then stored in glass bottles and kept at 4°C before analysis to determine the distribution of anionic surfactant and phosphate in the area of study. Meanwhile, for the photodegradation and coagulation experiments, artificial wastewater was used by preparing DBS and phosphate standard solutions.

2.2.2 Determination of DBS by UV/Visible spectrophotometric method

DBS in 5 mL of solution (or wastewater containing DBS) was reacted with 5 mL of MB solution to form colorless and insoluble DBS-MB complex. The complex was then extracted using 10 mL chloroform, resulting in the appearance of a blue solution. The blue solution in the chloroform was separated from the water phase by means of separation funnel. Then the absorbance of the organic solution was measured with Visible spectrophotometer at wavelength of 652 nm.

2.2.3 Determination of phosphate by UV/Visible spectrophotometric method

In the ascorbic acid-molybdate method, orthophosphate reacts with molybdate to form phosphomolybdic acid. Phosphomolybdic acid is reduced by ascorbic acid to form a blue complex. For such determination, 5 mL of phosphate as PO_4^{3-} solution (or wastewater containing phosphate) was added with 0.1 mL ascorbic acid then mixed by shaking for 5 min. Then the solution was reacted with 0.1 mL of ammonium molybdate solution and blue solution was formed. The absorbance of the blue solution was measured at 880 nm.

2.2.4 Photodegradation of DBS in the waste water

The processes of DBS photodegradation were carried out in a closed reactor completed with a UV lamp. For this purpose, 50 mL of water sample was prepared in a flask and added with a certain amount of TiO2 powder. The sample was then put inside the reactor, irradiated with UV light and simultaneously stirred magnetically for a period of time. Afterwards, the suspension was filtered to separate the filtrate from TiO_2 solid. The filtrate was analyzed to determine the DBS left in the solution by means of spectrophotometric visible method with methylene blue (MB). To obtain the optimum reaction time for the photodegradation process, a batch experiment was performed in varying durations (0, 1, 3, 6, 10, 15, 24, and 50 h). Meanwhile, to obtain the optimum amount of photocatalyst, a batch experiment was performed in varying dose of TiO_2.(0, 10, 20, 30, 40, 50, and 60 mg).

2.2.5 Coagulation process of the waste water

In this process, 50 mL of water sample was added with coagulant of a certain mass. 3 types of coagulants was used separately ($CaCl_2$, $FeCl_3$, and Alum). Then the mixture was stirred quickly for 1-2 min, followed by slow stirring in varied time (10, 20, 30, 40, and 50 min), in order to obtain the optimum time of the process. The solution was then filtered to separate it from the coagulant, obtaining a clear solution. The clear solution was then analyzed using spectrophotometric methods as described in the procedure above.

3. RESULTS AND DISCUSSION

3.1 The Character of Laundry Wastewater

The character of the waste water from laundry activity is represented by anionic surfactant (DBS) and phosphate content. The result of the determination of DBS and phosphate concentration is illustrated in Fig. 1.

The figure shows that the content of anionic surfactants and phosphate in the laundry waste water is very high, much higher than the maximal level regulated by the Government that is 0.2 mg/L and 0.1 mg/L, respectively. The high content of the chemicals in the waste water is understandable since the waste water was taken from the washing of the cloth; it was not from the rinse step. Waste water from rinsing steps should have lower concentration, because the chemicals have been diluted by the rinse water. Since the laundry wastewater is disposed directly to the nearby river water, it will potentially pollute the river with chemical substances. Therefore, the development of a waste water treatment procedure prior to disposal is required to minimize contamination of the river, in particular from anionic surfactants and phosphate.
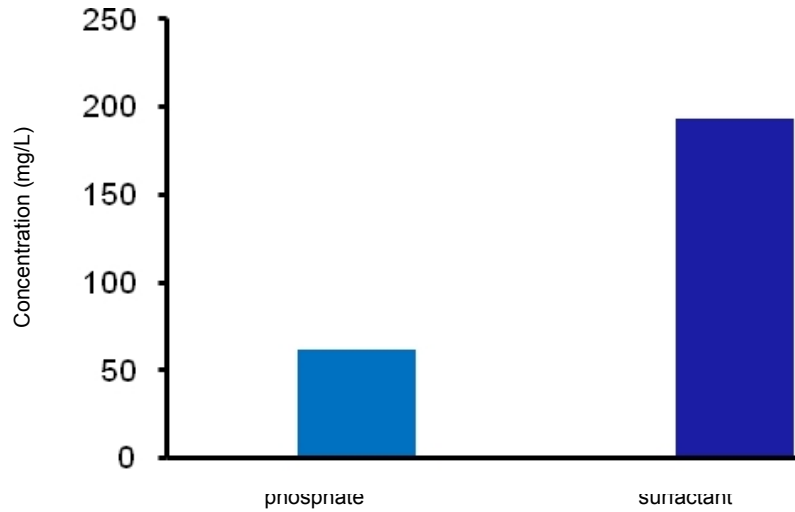
Fig. 1. The concentration of DBS and phosphate in the laundry wastewater

3.1 The Distribution of Anionic Surfactant (DBS) and Phosphate in Code River

The results of the determination of DBS and phosphate in the water samples are displayed in Fig. 2, while, the sampling points in Code River are illustrated in Fig. 3.
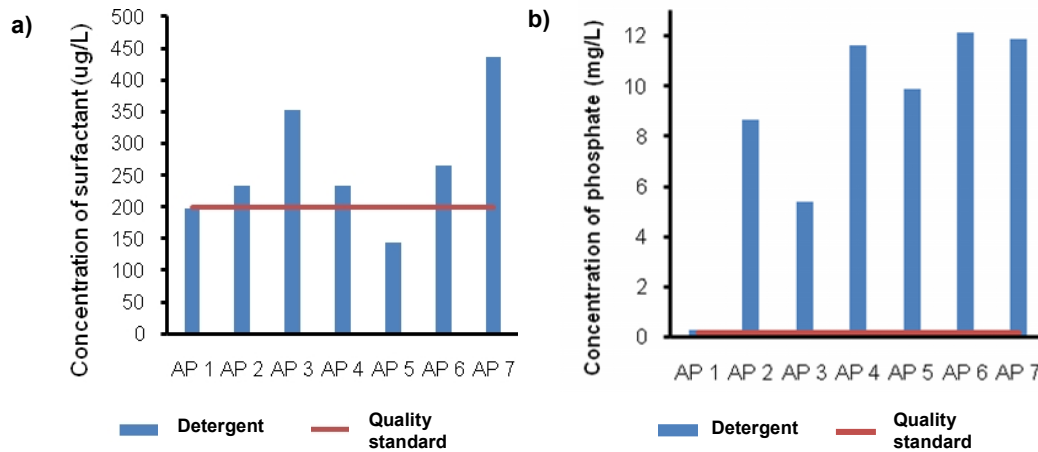

Fig. 2. The concentration of surfactant (a), and phosphate (b), in the River water samples
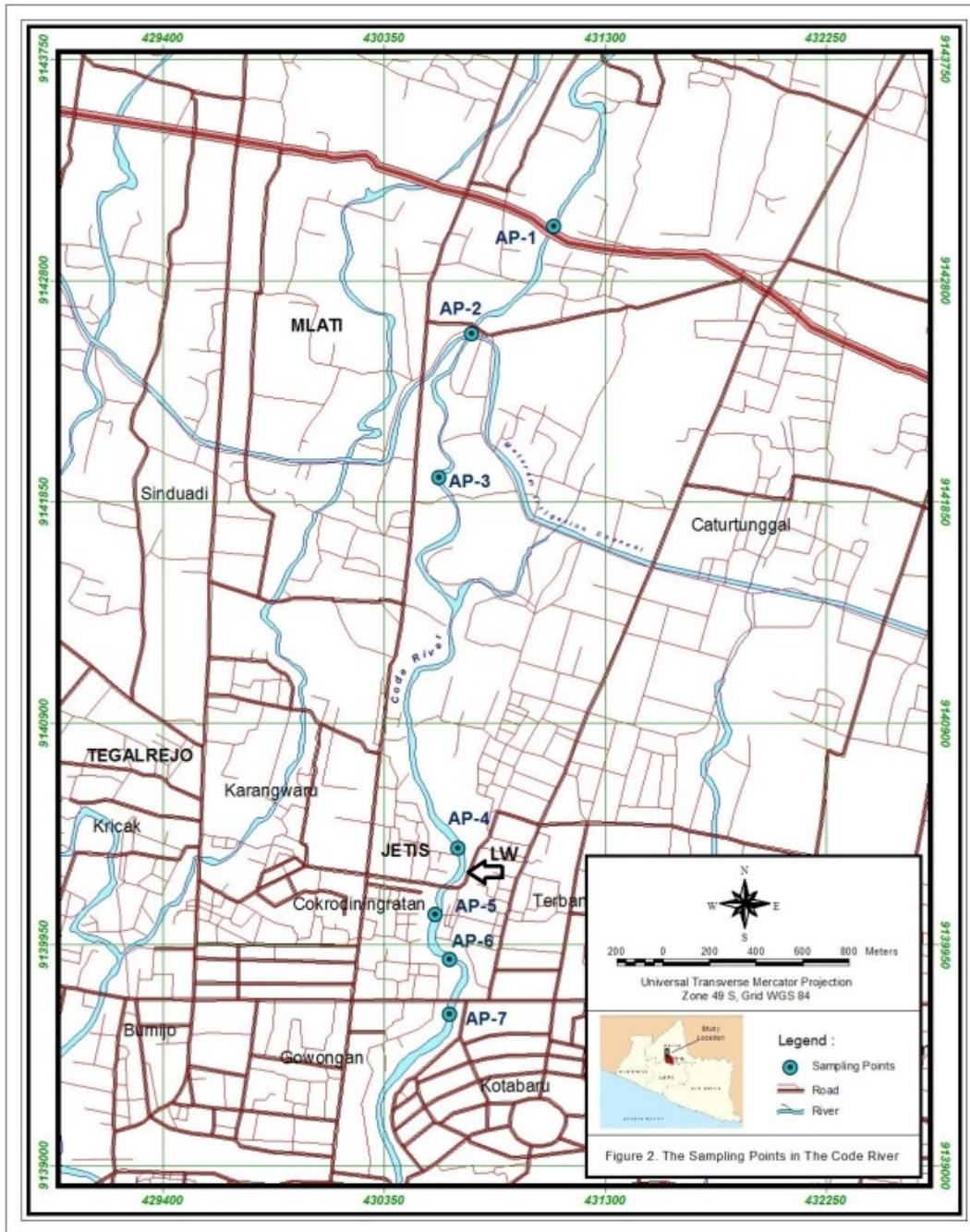
Fig. 3. The sampling points in Code River

The figures indicate that the water streams located before and after the point of the laundry waste water disposal site contain surfactant and phosphate with concentrations higher than the limit level of the standard quality. It is implied that the river has been contaminated by both chemicals, originating from domestic waste water around the river.

3.2 Photodegradation Process

The photodegradation experiments using TiO_2 as a photocatalyst were performed to suggest a wastewater treatment procedure in order to decrease the concentration of surfactants in receiving waters.
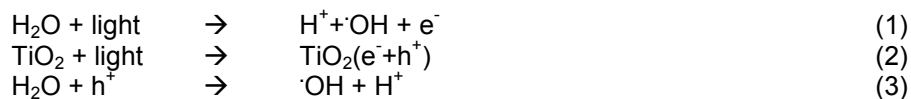
The TiO_2 was chosen in this study since it is a semiconductor that has a band gap [15], high activity and chemically stable [16]. To make sure that photodegradation of surfactants does occur by applying TiO_2, an experiment was performed to compare the removal of DBS in 3 different conditions: using UV light only, using TiO_2 without UV light, and using both UV light and TiO_2. The results are shown in fig. 4. The addition of TiO_2 without UV light treatment was able to remove 16% of DBS from the sample, indicating the occurrence of adsorption. However, when addition of TiO_2 was combined with UV light treatment, the removal of DBS reached 98%, indicating that photodegradation does occur significantly.
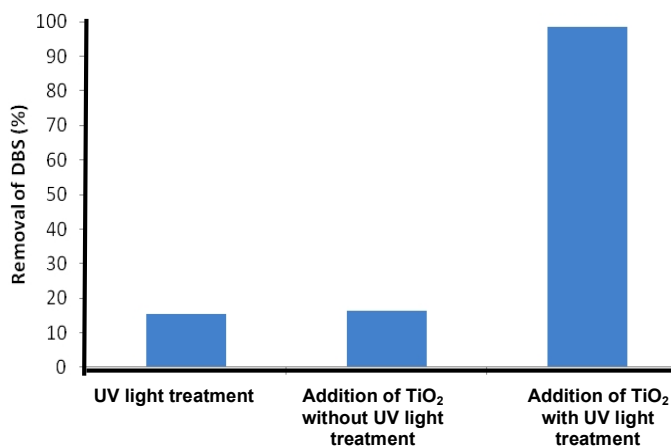

Fig. 4. The infuence of UV light treatment and the addition of TiO_2 on the removal of
DBS (DBS concentration: 10 ppm; TiO_2 mass: 10 mg; UV light treatment for 24 h)

In order to obtain optimum conditions for the photodegradation of surfactant in the water samples. The influence of photocatalyst dose and reaction time were studied. The results of the influence of reaction time are displayed in Fig. 5. From the figure, it is seen that the extended time up to 24 h give an increase in the photodegradation, but at longer reaction times the photodegradation remains constant. The longer the reaction time the higher the contact between surfactant with UV light and TiO_2, resulting in more effective contact. The more effective contact promotes higher photodegradation, and the surfactant can be completely photodegraded after 24 h.

When a solution containing DBS mixed with TiO_2 powder is exposed to UV light, H_2O as the media and TiO_2 can absorb the light while releasing electrons (e^-) accompanied by formation of positives (h^+) and $\cdot OH$ [17], as represented by reaction (1), (2), and (3).

$$H_2O + light \quad \rightarrow \quad H^+ + \cdot OH + e^- \qquad (1)$$
$$TiO_2 + light \quad \rightarrow \quad TiO_2(e^- + h^+) \qquad (2)$$
$$H_2O + h^+ \quad \rightarrow \quad \cdot OH + H^+ \qquad (3)$$

The radicals act as strong oxidizing agents, that can promote DBS oxidation followed by degradation to form smaller and safer molecules, as seen in reaction (4).

$$C_{12}H_{25}-C_6H_4-SO_3Na + {}^{\cdot}OH + h^+ \rightarrow \rightarrow CO_2 + H_2O + Na_2SO_4 \tag{4}$$
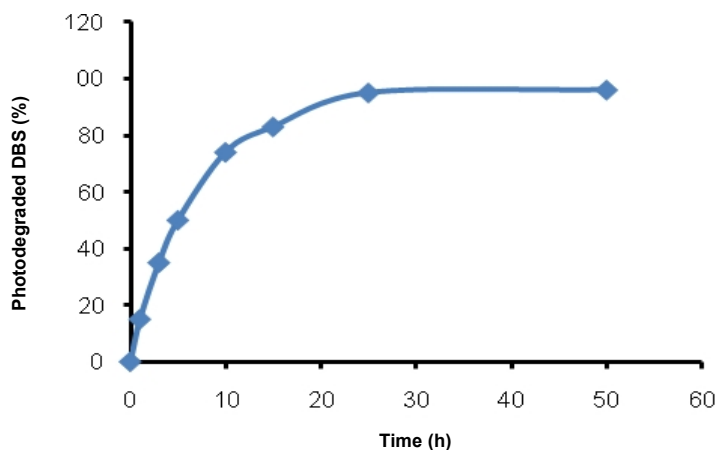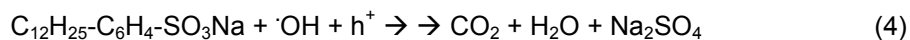
Fig. 5. The influence of the reaction time on the degradation effectiveness (concentration of TiO_2 is 10 mg in 50 mL of solution)

In addition to the reaction time, the photocatalyst dose is also examined and the results are presented in Fig. 6. The figure illustrates the improvement of the photodegradation along with the increase of the photocatalyst dose. However, after 30 mg, further increase of the photocatalyst dose leads to the decline of photodegradation. Increasing mass of TiO_2 can provide more amounts of ${}^{\cdot}OH$ that can induce more effective photodegradation. On the other hand very high mass of TiO_2 can increase the turbidity of the solution that can reduce the light entering the solution. Less intensity of the light entering the solution may result in less amounts of ${}^{\cdot}OH$. Consequently, the photodegradation becomes less effective.
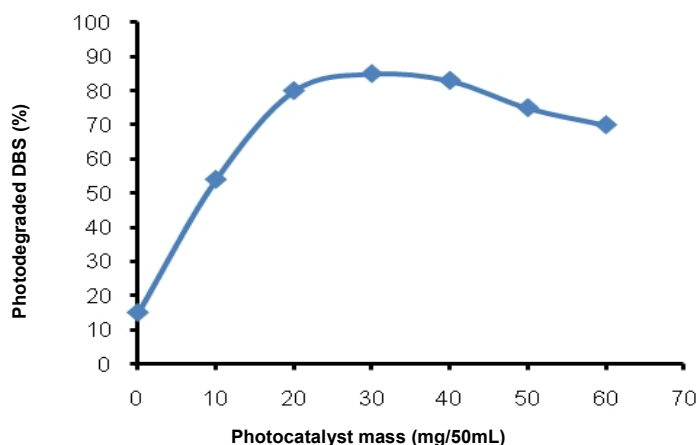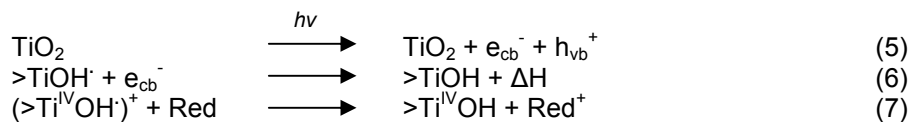

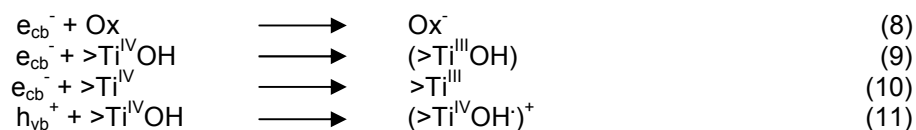**Fig. 6. The influence of photocatalyst dose on the surfactant photodegradation**

Moreover, when the semicondutor exposed with the light, that has the same energy or higher than the band gap, the electrons from the valence gap would excited to the

conduction gap by releasing a hole. The photocatalytic mechanisms on the TiO_2 surface is started with the formation of carriers charge by photon with *hv* energy, releasing a hole h_{vb}^+ on the valence gap followed by recombination of carriers charge and initiation of oxidation reaction on the band gap h_{vb}^+ using reductor (Red) substrat as presented in equation (5), (6) and (7).

$$TiO_2 \xrightarrow{\textit{hv}} TiO_2 + e_{cb}^- + h_{vb}^+ \qquad (5)$$

$$>TiOH^{\cdot} + e_{cb}^- \longrightarrow\ >TiOH + \Delta H \qquad (6)$$

$$(>Ti^{IV}OH^{\cdot})^+ + Red \longrightarrow\ >Ti^{IV}OH + Red^+ \qquad (7)$$

In addition, the next process, a photoreduction process, is release by performing initiation of reduction reaction by the electrons on the conduction gap e_{cb}^- using oxidation (Ox) substrat, followed with catalysed photodegradation and electrons as well as valence gap hole trapping processes to form of $^{\cdot}OH$ as displayed in equation (8), (9), (10) and (11) [17].

$$e_{cb}^- + Ox \longrightarrow\ Ox^- \qquad (8)$$

$$e_{cb}^- + >Ti^{IV}OH \longrightarrow\ (>Ti^{III}OH) \qquad (9)$$

$$e_{cb}^- + >Ti^{IV} \longrightarrow\ >Ti^{III} \qquad (10)$$

$$h_{vb}^+ + >Ti^{IV}OH \longrightarrow\ (>Ti^{IV}OH^{\cdot})^+ \qquad (11)$$

The symbol (>) represents the group is on the TiO_2 surface, while >TiOH is the main form of hydrated TiO_2 on the surface, $(>Ti^{IV}OH^{\cdot})^+$ and $(>Ti^{III}OH)$ are the trapped h_{vb}^+ and the trapped e_{cb}^- on the surface, respectively.

3.3 Coagulation Process

Coagulation by using salts of Al, Ca, and Fe is proposed for decreasing phosphate concentrations. The results of the coagulation process carried out at varied time are presented in Fig. 7.
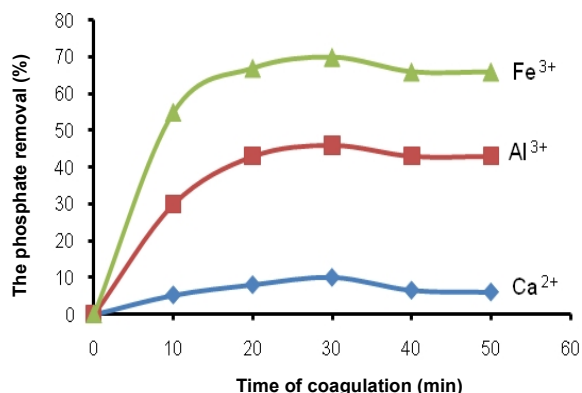
Fig. 7. The influence of the coagulation time on the phosphate removal
The figure shows that the improvement of the phosphate removal is observed when the coagulation time is extended up to 30 min, but the removal slightly decreases at longer time than 30 min. The extended time enables the phosphate to have more effective contact with the polycation of the coagulants, increasing the removal of phosphate. When the coagulation process is conducted longer than 30 min, the coagulants becomes exhausted, inhibiting the reaction with phosphate.

Moreover, form the figure it can be seen that the coagulation activity of Fe(III) in removing phosphate from the water sample is higher than Al(III). And the lowest activity is shown by Ca(II). The activity of a coagulant is determined by the poly nuclear formed. In the solution, Fe(III) is easier to form polynuclears than Al (III), while Ca(II) cannot become polynuclear. This explains the data obtained.

4. CONCLUSION

Laundry waste water analyzed in this study contains high surfactant and phosphate concentrations that are much higher than the limit level of applicable quality standard. The water streams in the Code River are found to be contaminated by surfactant and phosphate in low to medium level. The removal of the surfactant in the laundry waste water was successfully carried out by photodegradation method catalyzed by TiO_2, while the phosphate concentration can be decreased by coagulation method. The most effective surfactant removal is achieved by using 600 mg TiO_2 per L of waste water for 24 h of reaction time. The phosphate removal can be maximally removed in 30 min, and the highest activity for coagulation is shown by Fe(III) followed by Al(III) and Ca(II).

ACKNOWLEDGEMENTS

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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