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5 Degradation of linear alkylbenzene sulfonate (LAS) using TiO₂-chitosan composite as a photocatalyst

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Abstract. Linear Alkylbenzene Sulfonate (LAS) is an anionic surfactant that is widely used as an active ingredient in synthetic detergent formulation. Being a component in domestic waste, LAS can potentially be harmful to the environment. In this research, the degradation of LAS using TiO₂-chitosan composite as a photocatalyst was investigated. The optimum dose of TiO₂-chitosan to be used was determined, and the effect of pH towards the degradation effectiveness was also studied. The results showed that a dose of 1 g/100 mL composite at pH 6 gave an optimum result for the LAS degradation. In this optimum condition, the decrease in LAS concentration was up to 95.20% from its initial concentration.

1. Introduction

Linear Alkylbenzene Sulfonate (LAS) is one of the most common anionic surfactants that can be found as a component in commercial detergents. The use of LAS particularly increased after ABS (alkyl benzene sulfonates), another type of anionic surfactant, was banned due to its nature for being practically non-biodegradable [1]. Despite LAS being biodegradable in the environment, detergent wastewater that contains LAS still need to be properly treated before being released to the environment. This is because the degradation of LAS will not take place effectively in an anaerobic condition [2, 3]. Besides, high turbidity will also prevent the penetration of sunlight that slows down the degradation process [4]. In places with a high population density, domestic waste often contains a high load of detergent wastewater, and it tends to have very high turbidity [5]. Under this condition, the rate of LAS degradation in the domestic wastewater would be very low which might lead to a buildup of LAS concentration in the water to a toxic level. It has been reported that LAS concentration between 2-10 mg/L in the water can potentially be harmful to the aquatic organisms living in the polluted water [6].

Dealing with the negative impact of LAS in the environment, an effective treatment to remove LAS from the water is necessary. The use of photocatalyst, such as titanium oxide (TiO₂) to degrade LAS is an interesting option as it accelerates the degradation of LAS into non-harmful compound. Indeed, titanium dioxide has been widely used as a photocatalyst for various purposes due to its superior properties, such as high chemical stability and low toxicity [7]. Nevertheless, its application to treat wastewater still has some drawbacks. Because it is in the form of a fine powder, the recovery from the treated wastewater will be a difficult process. Moreover, adding a high dose of TiO₂ powder will cause an increase in turbidity and reduce the intensity of penetrating light needed for the photodegradation



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process of the targeted waste. To overcome these difficulties, TiO_2 is often immobilized into other materials as its solid support [8].

In this research, a composite material was prepared by immobilizing TiO_2 onto chitosan beads (CS). The TiO_2 /CS composite was then utilized to remove LAS from the solution. The effect of added dose and pH was investigated to find an optimum condition for LAS removal using this composite. As a comparison, LAS removal by photodegradation using TiO_2 powder and by adsorption using chitosan beads were also examined.

2. Materials and methods

2.1. Materials and instrumentation

Standard glasswares (Pyrex) were used in this research. The samples were illuminated using two 30W UV-lamps (Phillips) in a closed cabinet. The inner sides of the cabinet were covered with black plastic sheets to minimize light penetration from the outside. The chitosan used was food-grade chitosan (100 mesh, MW = 50,000-80,000 Da). Other chemicals used were TiO_2 powder, NaOH, linear alkylbenzene sulphonate (LAS) powder, H_2SO_4 , methylene blue solution, EDTA, CHCl_3 , HCl, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, CH_3COOH , and epichlorohydrin. All chemicals were reagent-grade from commercial sources (Merck) and used as received. UV-Vis analysis was done using Genesys 10S UV-VIS Spectrophotometer.

2.2. Preparation of TiO_2 /CS composites

Chitosan beads used in the composites were prepared based on the method suggested by Zhao, Xiao, Zhang, Su, & Tan [9]. Two grams of chitosan was dissolved in 100 mL 2% (w/w) aqueous acetic acid solution. After a 45-minutes of stirring, 0.4 grams of TiO_2 was added, followed by adding 1 mL of epichlorohydrin into the solution as a crosslinking agent. The mixture was continuously stirred for 5 hours. To form the desired beads, the chitosan solution was dripped into a 0.25 M NaOH solution using a dropping pipette. The formed beads were let to stay in the solution overnight, and then the beads were thoroughly washed using distilled water. The composites were put into a beaker containing 0.15% (w/v) EDTA solution and gently stirred for 4 hours, then the composites were washed using distilled water. Afterwards, the composites were put into a 0.05 M NaOH solution, stirred gently for two hours before rinsed with distilled water. The resulting TiO_2 /CS composites were filtered out and dried in the oven at 60°C . Some cross-linked chitosan beads (CS) were also prepared through the same procedure without the addition of TiO_2 in the process. To verify the immobilization of TiO_2 onto the chitosan beads in the composites, both the TiO_2 /CS composites and CS were analysed using FTIR Spectrophotometer.

2.3. Determination of the optimum dose

One hundred millilitres of LAS with a 100 ppm concentration was placed in a beaker glass. The desired amounts of TiO_2 /CS composites were added into the solution. In this study, three different doses of composites were used, i.e. 0.5, 1, and 2 grams of composites for 100 mL of LAS solution, and then the mixture was irradiated using the UV lamps in the closed cabinet for 5 hours. After the irradiation, the mixture was then centrifuged to separate the liquid phase from the composites. The liquid phase was withdrawn while the remained LAS concentration in it was analysed. The LAS concentration was analysed by MBAS methods, as suggested by the Standard Methods for the Examination of Water and Wastewater on anionic surfactant analysis. The same procedure was repeated using TiO_2 powder and CS with the same dose variations. To study the LAS removal through adsorption by CS, a set of experiments using CS where the LAS solution and CS were kept in a dark closed cabinet without UV irradiation was also conducted. This was to minimize the photodegradation process of LAS, so that the adsorption by CS became the dominant process taking place in the LAS removal.

2.4. Determination of optimum pH

One hundred millilitres of LAS with a 100-ppm concentration was placed in a beaker glass. The pH of the LAS solution was adjusted by adding 1 N NaOH or 1 N HCl, dropwise. The range of pH being studied in the research was from pH 2 to 10. After the desired pH was reached, TiO₂/CS composites were added into the solution. The amount of the composites added was fixed at the optimum dose that was determined based on the previous step. The same procedure of samples irradiation using UV lights and LAS analyses was repeated. Similar to the determination of the optimum dose, the determination of optimum pH was also conducted using TiO₂ powder and CS for both treatments with UV lamps and in the dark cabinet.

3. Results and discussion

3.1. FTIR analysis

To verify that TiO₂ had been successfully immobilized onto the chitosan beads, the functional groups of the TiO₂/CS and CS were analysed using FTIR spectrophotometer and compared to each other, along with the FTIR spectrum of TiO₂ powder. The FTIR spectra of TiO₂/CS, CS and TiO₂ powder are shown in figure 1.

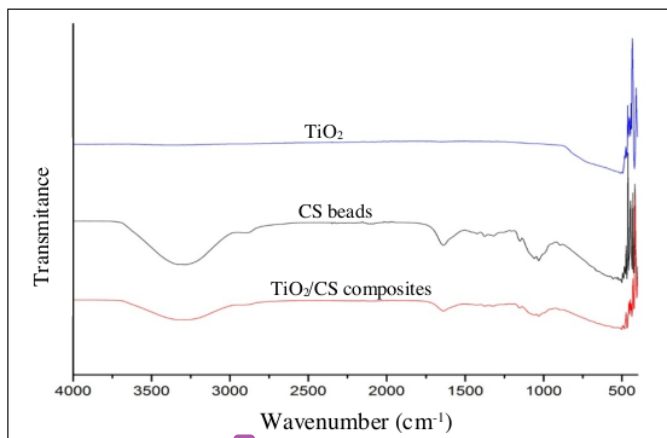


Figure 1. FTIR spectra of TiO₂, CS beads and TiO₂/CS composites.

From the figure, TiO₂/CS and CS appeared to have the same pattern. The peaks were around 3290 and 1650 cm⁻¹, and the characteristic of peaks for chitosan could be observed on the FTIR spectra of both TiO₂/CS composites and CS beads. However, TiO₂/CS spectrum showed peaks at wavenumbers that were less than 500 cm⁻¹ which were not present in the CS spectrum. These peaks came from TiO₂, an inorganic compound that did not give peaks at wavenumbers higher than 500 cm⁻¹, as shown in the spectrum of TiO₂ in figure 1. This confirmed that TiO₂ powder added in the composite preparation had been successfully immobilized into the structure of the chitosan beads. The TiO₂ might be attached on the chitosan beads through hydrogen bonding, as implied from a decrease of intensity at the peak around 3400 cm⁻¹.

3.2. Optimum dose

To determine an optimum dose in each treatment, various amounts of composite, CS beads, and TiO₂ powder were added into 100 mL LAS solution, where the initial LAS concentration was 100 ppm. The results are displayed in figure 2 that shows the decrease of LAS concentration in the solution as a function of the dose being added to the solutions.

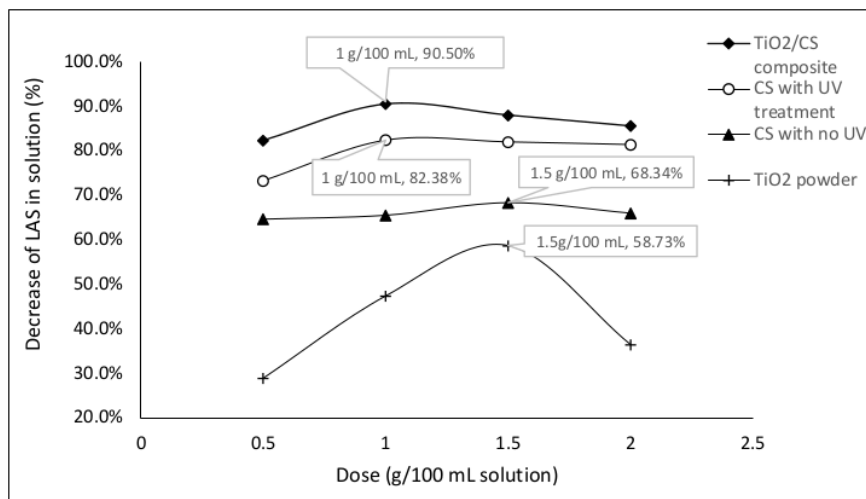


Figure 2. The decrease in LAS concentration for each treatment with various doses.

From the figure, it can easily be observed that TiO₂/CS showed the best result in decreasing the LAS concentration from the solution. One gram of TiO₂/CS composites in a 100 mL sample was enough to remove 90% LAS from the solution. A higher dose did not increase the removal percentage significantly, implying that a 1 g composite/100 mL sample was enough to have an optimum result. It is interesting to note that the LAS removal appeared to be more effective through adsorption instead of the photodegradation. This was indicated by a better removal percentage when the LAS solution was treated with CS, even when the mixture was kept in a dark cabinet with a minimum exposure to light. The optimum result obtained was a 58.73% removal of LAS when LAS solution was treated by TiO₂ powder which was reached when using 1.5 grams of TiO₂ powder for a 100 mL solution. When CS was used and the solution was kept in a dark cabinet, the LAS removal was up to 68.34% from the initial concentration. This result shows a considerably lower value than a study conducted by Kumiyati, Sumarni, & Latifah [10]. They reported that chitosan bead was able to reduce the concentration of ABS, another type of anionic surfactant, up to around 90% from its initial concentration. However, their result which showed a higher removal was probably because their study was not set up in a condition where the UV light was minimized and, thus, enabled a surfactant removal through the photodegradation process.

Nevertheless, the presence of UV light is also able to remove LAS from the solution as it facilitates the photodegradation of LAS. This was indicated by the increase in LAS removal when the solution was treated with CS beads and irradiated with UV lights. It can be deduced that the LAS removal occurred not only through adsorption by the CS beads, but also through the photodegradation process by the UV light. As shown in figure 2, not only the LAS removal increased up to 82.38%, but this optimum result also came with a lower dose of beads. The addition of TiO₂ into the chitosan beads enhanced the LAS removal by catalysing the photodegradation of LAS. This result corresponds to the report by Zainal, Hui, Hussien, & Abdullah [11] who pointed out that removal of contaminants using a TiO₂-chitosan composites would occur through adsorption and photodegradation. Meanwhile, it has to be noted that in other treatments, a higher dose than the optimum one no longer increased the LAS removal when it came to the treatment with TiO₂. An excessive dose leads to a quite significant decrease in its efficiency to remove LAS. Since TiO₂ powder is practically insoluble in water, a high load of TiO₂ in water would make the particles being suspended in it then blocked UV lights from

penetrating the solution. As highlighted by Kansal, Ali, & Kapoor [12], a high load of TiO_2 will reduce the effectiveness of photodegradation process as the UV light is scattered by the TiO_2 particles.

3.3. Optimum pH

It has been reported that pH often plays a key role in waste removal, including in treatment using photocatalysts. This is mainly because pH will determine the compound species present in the system and, thus, it will influence the interaction between said species and the photocatalysts [13]. In this study, after the optimum dose had been determined, the study was repeated by using the optimum dose for each treatment but at various pH. The result is presented in figure 3, where the removal of LAS is shown as a function of the solution pH.

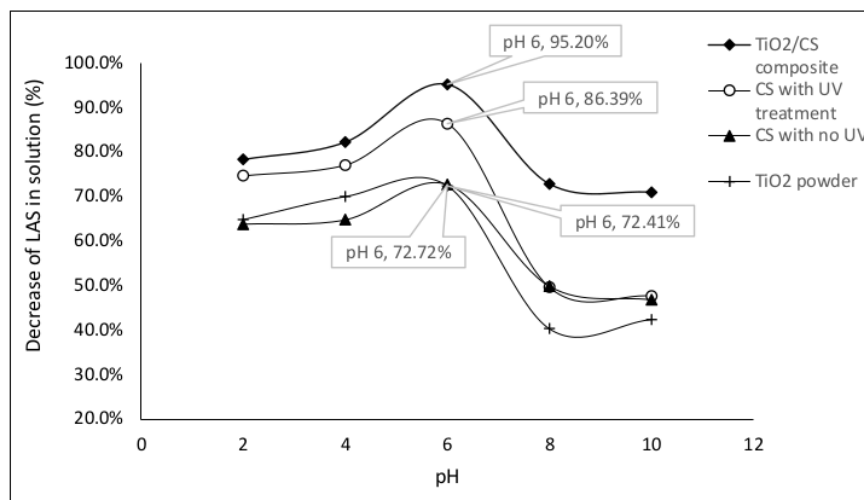


Figure 3. The decrease in LAS concentration at different pH.

Similar to the previous results, the highest percentage of LAS removal from the solution was achieved when LAS was treated using TiO_2/CS composites. All of the treatments gave optimum results at pH 6. A higher pH led to a performance drop for all of the treatments quite significant. The effect of pH can be explained by how CS and TiO_2 become positively charged in an acidic pH. Due to the presence of its amine groups, CS will become a polycationic in an acidic pH as the amine groups are protonated, making them available to have electrostatic interaction with LAS [14]. The surface of TiO_2 also becomes negatively charged in an acidic pH, facilitating the adsorption of LAS onto it [15]. However, as indicated from a lower LAS removal in a lower pH, it appeared that when the pH was too low, there would be a competition between the positive charges of CS and the TiO_2 surface with the excessive proton to interact with LAS molecules. Hence, a slightly acidic pH (pH \approx 6) is a favourable condition to have an optimum result. When pH is alkaline, the amine groups in CS are less protonated, and makes it less effective to adsorb LAS molecules. The same thing occurs for the TiO_2 case. In alkaline pH, the surface of TiO_2 will be negatively charged which leads to repulsion forces between it and the LAS molecules. It is also worth to note that the attachment of LAS to the surface of TiO_2 seemed to play an important role in the photocatalytic degradation of LAS. In figure 2 where the pH of the solution was not adjusted (pH \approx 7.5), the LAS removal was much lower than when the pH was adjusted to be slightly acidic (pH \approx 6). At the optimum pH, the LAS removal by TiO_2 powder through photodegradation process was up to 72.41% from its initial concentration. Under this condition, the LAS removal through the photodegradation process was even as effective as adsorption by CS

conducted in a dark closed cabinet (72.72%). The same pattern can also be observed in a treatment using TiO₂/CS composite where a slight adjustment of pH can enhance the LAS removal effectiveness.

4. Conclusion

From this study, it can be concluded that TiO₂/CS composite is a potential material to be used in removing LAS from solution. The composite gave a better result than when the LAS solution was treated with TiO₂ powder and CS beads, as the removal took place through adsorption and photocatalytic degradation. The removal of LAS in this study was highly influenced by pH, and the optimum results were achieved at pH 6, or a slightly acidic pH. A dose of 1-gram composite per 100 mL solution at pH 6 was enough to remove LAS up to 95% from its initial concentration.

References

- [1] Scheibel JJ 2004 The evolution of anionic surfactant technology to meet the requirements of the laundry detergent industry *J Surfactants Deterg* **7(4)** 319-28
- [2] Cowan-Ellsberry C, Belanger S, Dorn P, Dyer S, McAvoy D, Sanderson H, Versteeg D, Ferrer D, Stanton K 2014 Environmental safety of the use of major surfactant classes in North America *Crit Rev Env Sci Tec* **44(17)** 1893-993
- [3] Scott MJ and Jones MN 2000 The biodegradation of surfactants in the environment *Biochim Biophys Acta* **1508(1)** 235-51
- [4] Oyama T, Aoshima A, Horikoshi S, Hidaka H, Zhao J and Serpone N 2004 Solar photocatalysis, photodegradation of a commercial detergent in aqueous TiO₂ dispersions under sunlight irradiation *Sol Energy* **77(5)** 525-32
- [5] Abd El-Gawad HS 2014 Aquatic environmental monitoring and removal efficiency of detergents *Water Science* **28(1)** 51-64
- [6] Steber J 2007 The ecotoxicity of cleaning product ingredients in *Handbook for Cleaning/Decontamination of Surfaces* ed Johansson I and Somasundaran P (Amsterdam: Elsevier) pp 721-746.
- [7] Daghrir R, Drogui P and Robert D 2013 Modified TiO₂ for environmental photocatalytic applications: a review *Ind Eng Chem Res* **52(10)** 3581-99
- [8] Khataee AR, Fathinia M, Aber S and Zarei M 2010 Optimization of photocatalytic treatment of dye solution on supported TiO₂ nanoparticles by central composite design: intermediates identification *J Hazard Mater* **181(1-3)** 886-97
- [9] Zhao X, Xiao G, Zhang X, Su H and Tan T 2012 The effect of Ni²⁺ and Cu²⁺ on the photocatalytic degradation of dyes by the chitosan-TiO₂ complex *Appl Biochem Biotech* **168(1)** 183-97
- [10] Kurniyati R, Sumarni W and Latifah L 2015 Pengaruh chitosan beads dan chitosan beads ikat silang asam sitrat sebagai penurun kadar fosfat dan ABS (Alkyl Benzene Sulfonate) pada limbah laundry, " *Indo J Chem Sci* **4(1)** 36-41
- [11] Zainal Z, Hui LK, Hussein MZ and Abdullah AH 2009 Characterization of TiO₂-chitosan/glass photocatalyst for the removal of a monoazo dye via photodegradation-adsorption process *J Hazard Mater* **164(1)** 138-45
- [12] Kansal SK, Ali AH, Kapoor S 2010 Photocatalytic decolorization of bieberich scarlet dye in aqueous phase using different nanophotocatalysts *Desalination* **259(1-3)** 147-55
- [13] Akpan UG and Hameed BH 2009 Parameters affecting the photocatalytic degradation of dyes using TiO₂-based photocatalysts: a review *J Hazard Mater* **170(2-3)** 520-29
- [14] Ngah WW, Teong LC and Hanafiah MM 2011 Adsorption of dyes and heavy metal ions by chitosan composites: A review *Carbohyd polym* **83(4)** 1446-56
- [15] Gaya UI and Abdullah AH 2008 Heterogeneous photocatalytic degradation of organic

contaminants over titanium dioxide: a review of fundamentals, progress and problems *J Photoch Photobio C* **9(1)** 1-12

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