Jurnal Kimia Valensi, Vol 5(2), November 2019, 177-184
Available online at Website: http://journal.uinjkt.ac.id/index.php/valensi

Ag_3PO_4-Red Banyan Fruit Extract (*Ficus benjamina.* L) Nanocomposite for Degradation of Detergent Waste

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Received: July 2018; Revision: August 2018; Accepted: October 2019; Available online: November 2019

Abstract

Detergents waste containing SDS (*Sodium Dodecyl Sulfate*) still becomes a major environmental problem that must be overcomed. The degradation of SDS by silver phosphate (Ag_3PO_4)-Red Banyan extract nanocomposite was performed under visible light. This research aimed to determine the percentage decrease in SDS concentration under visible light by using Ag_3PO_4 facilitated extract of red banyan fruit. The Ag_3PO_4-Red Banyan extract nanocomposite was prepared by coprecipitation method and facilitated by a red banyan extract solvent. The result showed that the silver composite phosphate (Ag_3PO_4) facilitated red banyan extract had a percentage of SDS degradation i.e. 85.9% for 2 hours. This result showed that the silver composite phosphate (Ag_3PO_4)-a red fruit extract becomes a promising ingredient for degrading SDS in aquatic environment environments.

Keywords: Silver Phosfate (Ag_3PO_4), SDS (*sodium dodecyl sulfate*), degradation, red banyan fruit.

Abstrak

Limbah deterjen yang banyak mengandung SDS (*Sodium Dodecyl Sulfate*) masih merupakan masalah lingkungan yang perlu diatasi. Degradasi SDS oleh komposit perak fosfat (Ag_3PO_4)-ekstrak buah beringin merah di bawah sinar tampak telah dilakukan. Tujuan dari penelitian ini adalah untuk mengetahui persentase penurunan SDS di bawah sinar tampak dengan menggunakan komposit perak fosfat (Ag_3PO_4) terfasilitiasi ekstrak buah beringin merah.Komposit perak fosfat (Ag_3PO_4) dibuat dengan metode kopresipitasi dan terfasilitasi oleh pelarut ekstrak buah beringin merah. Hasilnya menunjukkan bahwa komposit perak fosfat (Ag_3PO_4) terfasilitiasi ekstrak buah beringin merah memiliki persentase degradasi terhadap SDS yakni 85.9% selama 2 jam. Hasil ini menunjukkan bahwa komposit perak fosfat (Ag_3PO_4)-ekstrak buah beringin merah menjadi bahan yang menjanjikan untuk mendegradasi di lingkungan perairan.

Kata kunci: Perak fosfat (Ag_3PO_4), SDS (*sodium dodecyl sulfate*), degradasi, buah beringin merah.

DOI: *10.15408/jkv.v5i2.8390*

1. INTRODUCTION

The development of a country is always accompanied by the development of industry, both large industries and small industries (households). Along with these developments, it turns out that progress in terms of industry does not always produce positive things. One of the developing industries, especially in urban areas, is a home industry such as laundry. It is undeniable that more laundry service would produce more water pollution by chemicals (such as detergents) The use of detergents is increasingly widespread because detergents have effective cleaning properties compared to ordinary soap. In detergents, there are materials that have surface-active properties (surfactants). Surfactants are used for the binding process of impurities so that the nature of the detergent can differ depending on the type of surfactant. Detergents that are sold freely on the market usually contain 20-40% surfactants, while the rest are chemicals that are usually called additives or detergent

P-ISSN: 2460-6065, E-ISSN: 2548-3013

builders that function to increase the detergent's clean power (Santi, 2009).

Based on the decree of the minister of health No: 416/MEN.KES/PER/IX/1990 concerning the requirements and supervision of water quality, only 0.5 mg/L of detergents are allowed in drinking water. The increasing use of detergent causes surfactant waste to increase in water which can damage both health and the environment. The impact of high levels of waste can cause skin irritation, itching, damage to internal organs, the formation of film that causes a decrease in the level of transfer into the water, as well as the combination of polyphosphate with surfactants in detergents can increase the phosphate content in water. It will lead to eutrophication that can cause color in water (Santi, 2009).

With a deteriorating environment and a growing energy crisis worldwide, semiconductor photocatalysts have attracted widespread attention for potential applications such as degradation of organic pollutants, decomposition of H_2O to H_2, and CO_2 photoreduction (Li, 2017). Photocatalysis is a promising technology that can be used as an important toolkit for overcoming the global energy crisis and overcoming many environmental problems (Agbe, 2018). Photocatalyst material has long been used in various fields both in daily life or industry today. Photocatalyst is a material that uses light or photons to activate themselves in the process of excitation of electrons from the ground state (valence band) to a higher state or greater energy (conduction band). This process is utilized in various fields such as in the self-cleaning process or in further applications such as self-sterilizing to decrease pollutants in free air and harmful microorganisms (Wibowo, 2014).

The presence of silver phosphate photocatalysts (Ag_3PO_4) has been a focus of attention for researchers in recent years because generally photocatalysts currently in circulation such as TiO_2 are limited to a few days, including a wide bandgap energy of 3.18 eV for anatase and 3.02 for rutile (Cui *et al.*, 2015) makes it active only in UV light where the portion of UV light is only about 3-5% of the spectrum of light that can be absorbed, the slow rate of separation from TiO_2 photoexcitation shows the limitations of its quantum efficiency and others (Syam, 2014).

Ag_3PO_4 photocatalyst is a photocatalyst that is able to absorb visible light (Liu *et al.*, 2011), has excellent photooxidative ability to split water into O_2 molecule, has high photocatalytic activity for the degradation process in various types of pollutants (Cao *et al.*, 2018), and has a quantum efficiency approaching 90% under visible light irradiation (Yi *et al.*, 2010). Silver phosphate (Ag_3PO_4) is a new semiconductor photocatalyst that has a strong absorption ability as well as its ability to utilize visible light with wavelengths lower than 530 nm (Chenfan, 2017). This research was conducted to increase the degradation activity of silver phosphate (Ag_3PO_4) by utilizing red banyan fruit extracts as sensitized, so that it can increase its activity in degrading waste and stable in the process of biochemical and chemical processes.

2. MATERIALS AND METHODS

Instruments and Materials

The following tools and materials were used in this research namely UV-Vis Spectrophotometer (Jasco V-630), FT-IR Spectrophotometer (Shimadzu FTIR-8201 PC), SEM-EDX (TESCAN-BRUKER), glassware (pyrex), paper filter, detergent waste from the local laundry service business in Kendari, $AgNO_3$ (Smart-Lab), KH_2PO_4 (Emsure Merck), distilled water, ethanol 70% (One Med), and SDS (Emsure Merck).

Red Banyan Fruit Preparation

Red banyan fruit that has been taken, dried in advance by drying. Furthermore, the sample was cut into small pieces then the sample was mashed.

Red Banyan Fruit Extraction

Maceration, immersion with organic solvents at room temperature, was used to extract Red Banyan sample. A total of 200 grams of red banyan fruit samples were macerated with 800 mL of 70% ethanol in a 1000 mL beaker. The suspension was closed and shaken for ±4 hours. The suspension was filtered, the filtrate was collected in vial.

Synthesis of Ag_3PO_4 Composites-Red Banyan Fruit Extract

Ag_3PO_4 composite-red banyan fruit extract was made by reacting a solution of KH_2PO_4 and $AgNO_3$ which has been dissolved in red banyan fruit extract with 10 mL and 20 mL. Ag_3PO_4 photocatalyst-Red banyan fruit extract was made by mixing 10 mL of $AgNO_3$ solution into 20 mL of KH_2PO_4 solution then a magnetic stirrer was used to stir the solution until the mixture homogenous. The resulting precipitate was filtered using a filter paper, washed with demineralized water and dried in an oven for 2 hours at 60 ^oC.

SDS Degradation Test

In this research, SDS was used as a degredation compound found in detergents. Test performance of silver sulfate composites from red banyan fruit extracts was carried out for its activity in degrading SDS compounds. 300 mg of photocatalyst material and 400 mL of SDS compound were put into a beaker and degraded at intervals of 30 minutes, 60 minutes, 90 minutes and 120 minutes with visible radiation while homogenized with magnetic stirrers. The changes in SDS concentrations were analyzed using the UV-Vis spectrophotometer. Next, Equation 1 was used to determine the percentage of SDS degradation.

$$\%D = \frac{C0\text{-}Ct}{C0} \times 100\% \qquad (1)$$

Where:
%D = Percentage of SDS degradation
C_0 = initial concentration of SDS
C_t = final concentration of SDS

3. RESULTS AND DISCUSSION

Initial Sample Preparation Results

In this study, Red Banyan fruit was collected from collected from the Forest Park of the University of Halu Oleo, Kendari, Southeast Sulawesi. The Samples were prepared by washing with distilled water so that contaminants such as dust, would not affect the extract obtained from this fruit. Samples were mashed to streamline, and then the sample many secondary metabolites can be extracted. The extraction technique used was maceration or immersion with organic solvents, in this case the solvent used was ethanol at room temperature. As for the advantages of choosing this technique, which is not only easy to do, soaking process will also accelerate the breakdown of cell walls and membranes as a result of differences in pressure inside and outside the cell which causes secondary metabolites in the cytoplasm to dissolve in organic compounds making it easier in the extraction process.

Synthesis of Silver Phosphate Composite (Ag_3PO_4) - Red Banyan Fruit Extract

The silver phosphate composite (Ag_3PO_4) facilitated by the red banyan fruit extract solvent has been successfully synthesized as indicated by the formation of yellow powder. The mass of silver phosphate composite (Ag_3PO_4) formed was 0.3 grams with with 71.6% yield was obtained.

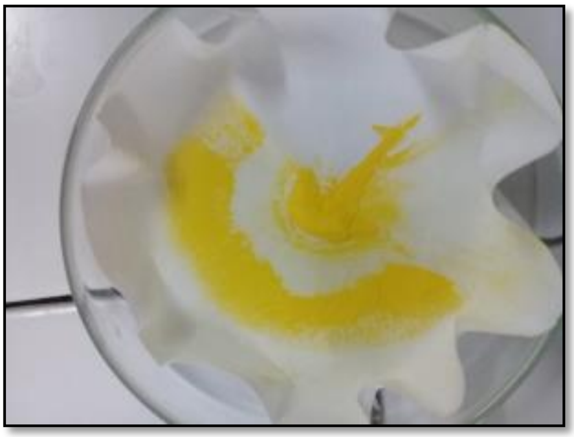

Figure 1. Silver Phosphate Composite (Ag_3PO_4) Red Banyan Fruit Extract

Characteristics of Ag_3PO_4 Composite-Red Banyan Fruit Extract

Functional Group Analysis Using FTIR

Functional group analysis is one way to determine the chemical characteristics and success of silver phosphate (Ag_3PO_4) composite synthesis-red banyan fruit extract by FTIR method. The FTIR spectrum for red banyan fruit and silver phosphate composites (Ag_3PO_4) - red banyan fruit extract is shown in Figure 2.

Based on Figure 3 (b) it can be seen that the FTIR spectrum of the red banyan fruit shows the presence of O-H, C=C, C-O and aromatic ring groups. The FTIR spectra interpretation shows OH functional groups shown by sharp absorption in the region of wave number 3408.22 cm^{-1} (Chen *et al.*, 2018) which is supported by the emergence of wave number 1070.49 for CO bonds (Miao *et al.*, 2018) and absorption in wave numbers 1724.36.49 cm^{-1} for the C=O bond. The shift of the wavenumber in the C=O group wherein the red banyan fruit is found in the wavenumber 1724.36 cm^{-1} whereas in the silver phosphate composite (Ag_3PO_4)-red banyan fruit extract is found in the wave number 1656.85 cm^{-1} . Both of these wave numbers are characteristic of the C=O functional group, but the difference is the absorption of the wave number 1724.36 cm^{-1} which corresponds to saturated aliphatic functional group, while characteristic of the stretching of the saturated aliphatic function group while the wave number 1656.85 cm^{-1} is a characteristic of the aromatic function group stretching ketone. Figure 3 (a) shows the absorption of the wave number 540.07 cm^{-1} which indicates the bending vibration of O=PO (Guy *et al.*, 2018), while at the peak of the wave number 856.39 cm^{-1} is symmetrical and asymmetrical vibrations from POP (Zhang *et al.*, 2018). Based on the results of FTIR spectra interpretation, it can be concluded that the silver phosphate composite (Ag_3PO_4)-red banyan fruit extract has been successfully synthesized by the coprecipitation method.

Morphological Analysis Using SEM-EDX

SEM characterization is useful to determine the morphology, porosity and thickness of a material and is also equipped with EDX which can detect elements in the sample and also the surface observed through the conductor of electrons. Analysis using SEM (Scanning Electron Microscopy) was conducted to determine the particle size of silver phosphate composites (Ag_3PO_4) which was synthesized using red banyan fruit extracts and compare them with particle size of silver phosphate composites (Ag_3PO_4) synthesized using 10.000 times more distilled water.

Based on the scanning electron microscope analysis, Ag_3PO_4 facilitated the red banyan fruit extract solvent to have a smaller size than Ag_3PO_4 which was synthesized using only water solvents without the facilitated red banyan fruit extract (Figure 3) its photocatalytic activity can increase (Yan *et al.*, 2017). Analysis using EDX (Energy Dispersive X-Ray) was carried out to determine the elemental content of the silver phosphate composite (Ag_3PO_4) which was synthesized using red banyan fruit extract and silver phosphate nanocomposite (Ag_3PO_4) which was synthesized in distilled water.

Based on the analysis using Ag_3PO_4 EDX (Energy Dispersive X-Ray) facilitated the red banyan fruit extract solvent contains the more dominant Ag and P elements compared to silver phosphate composites (Ag_3PO_4) synthesized using distilled water. As for the element C it can be associated with resin conductive (Xie *et al.*, 2018).

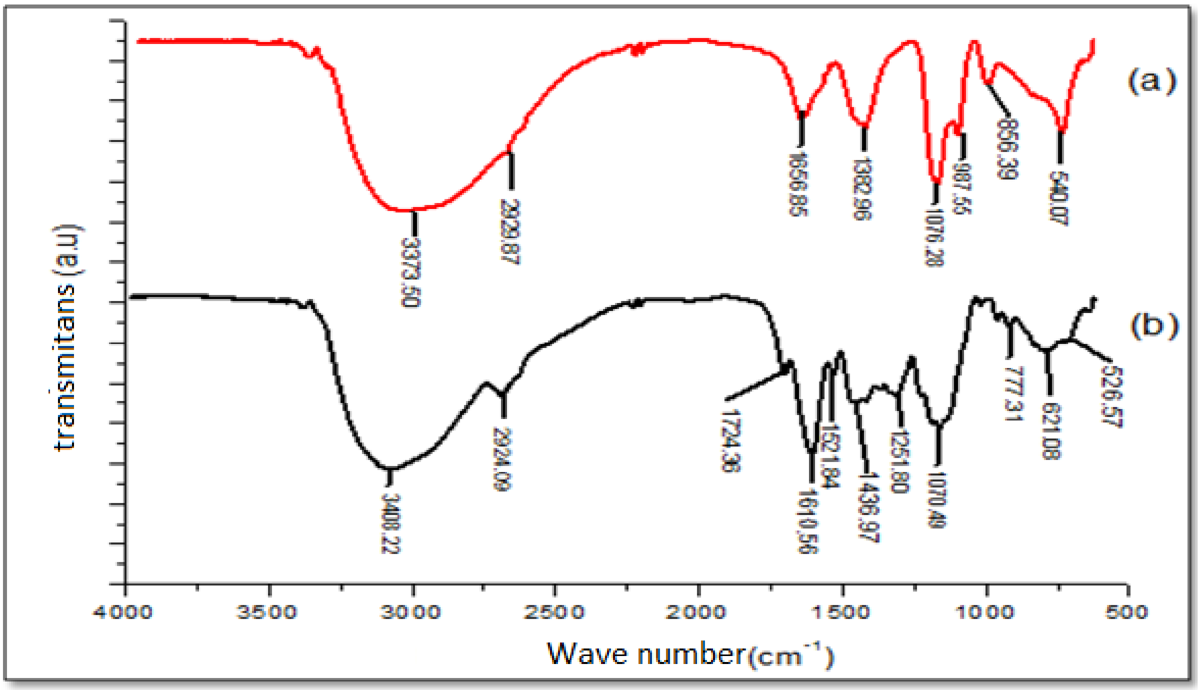

Figure 2. (a) FTIR spectrum of Ag_3PO_4-red banyan fruit extract nanocomposite (b) FTIR spectrum of red banyan fruit.

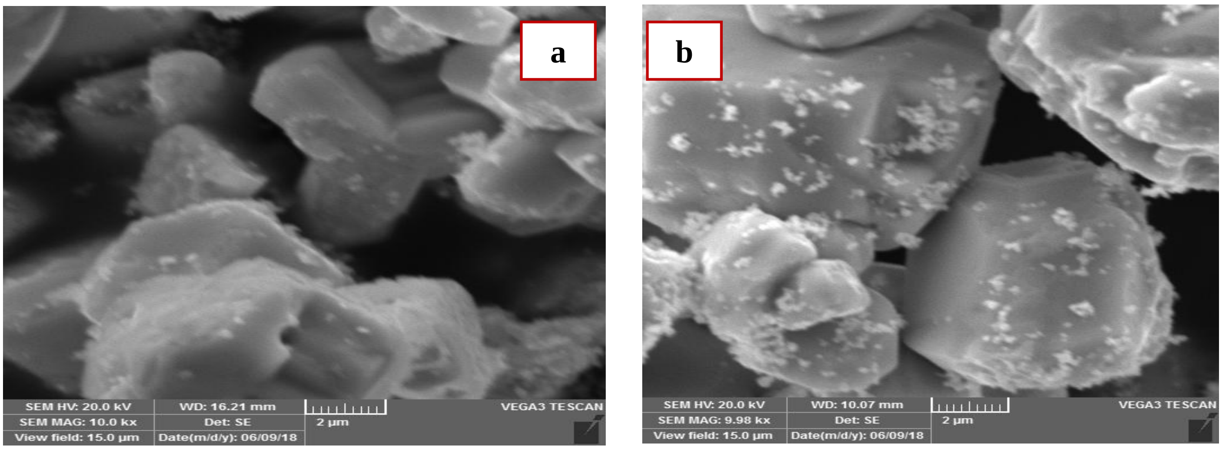

Figure 3. (a) Morphology of Ag_3PO_4-red banyan fruit extract nanocomposite (b) morphology of Ag_3PO_4 without facilitated red banyan fruit extract.

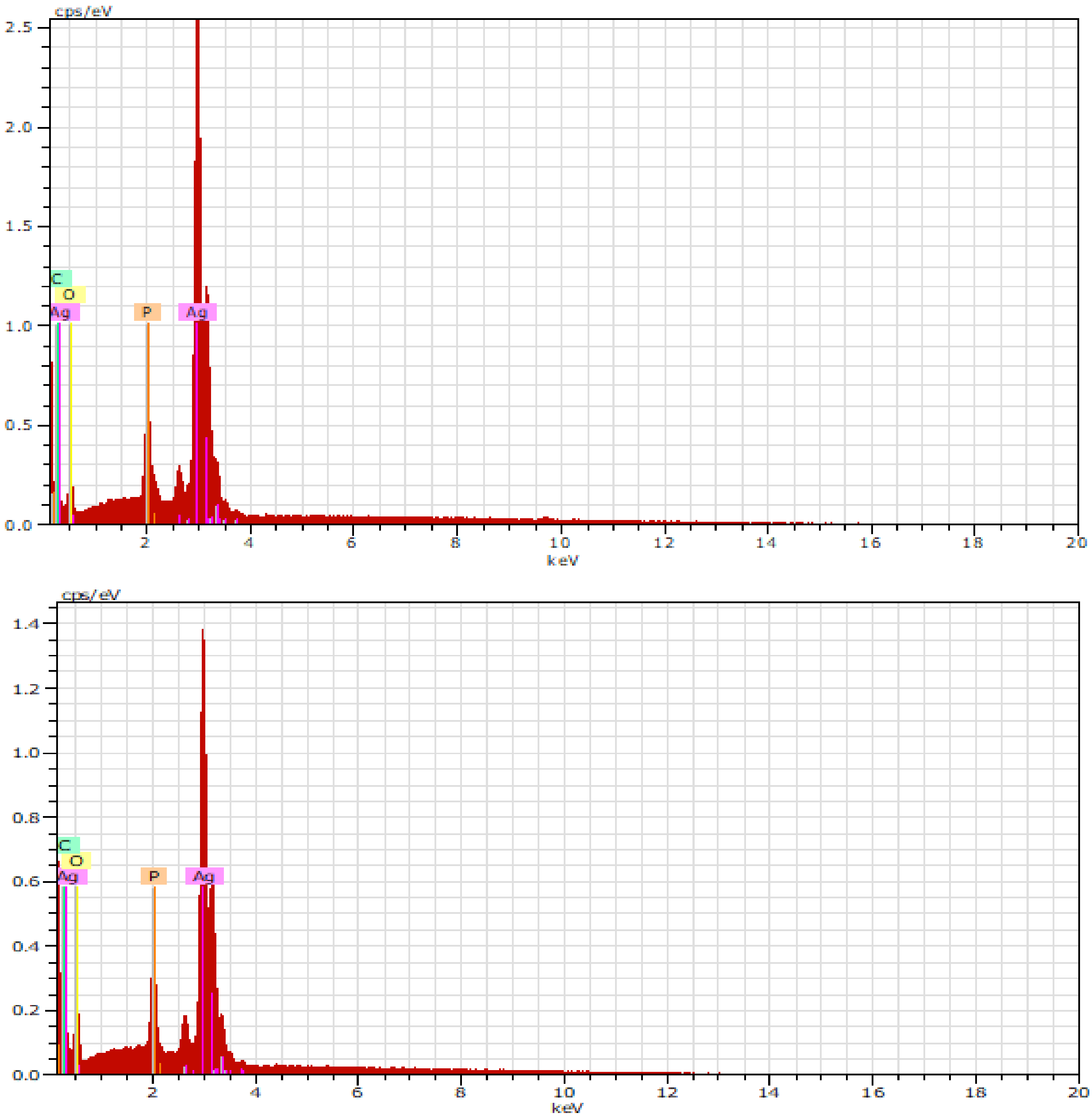

Figure 4. (a) Ag_3PO_4-red banyan fruit extract nanocomposite, (b) silver phosphate (Ag_3PO_4).

SDS Degradation Testing

Determination of Maximum Wavelength and Manufacture of SDS Standard Curves

The maximum wavelength of SDS obtained is 652 nm. SDS standard curves were plotted based on comparison of concentration and absorbance data released by the UV-Vis spectrophotometer resulting in a linear regression equation y = 0.0739x + 0.0088 with a coefficient of determination (R2) = 0.9631. The correlation coefficient is close to 1, and then the equation can be used to determine the concentration of SDS after the photodegradation process.

Table 1. Absorbance of SDS standard solution

Number	SDS (*Sodium Dodecyl Sulfate*) Standard Concentration, ppm	Absorbance (A)
1	0.4	0.045
2	0.8	0.077
3	1.2	0.099
4	1.4	0.104

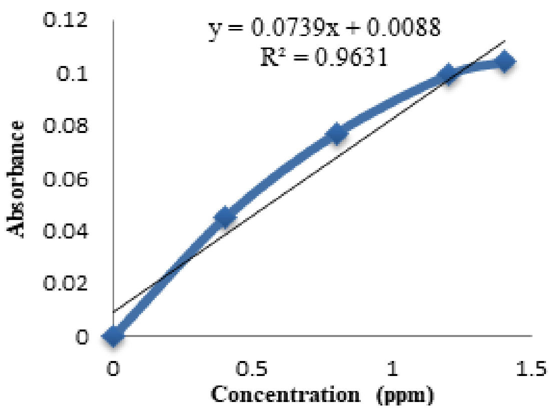

Figure 5. SDS standard curve graph

Nanocomposite Performance Against SDS Degradation

The photocatalysis process is one of the degradation processes that uses catalysts and photon assistance. The reactions that take place in solution result in the formation of hydroxyl radicals (•OH) due to H_2O oxidation by holes. In addition, the presence of dissolved O_2 in water triggers the formation of superoxide radicals (• O_2^-) due to the reduction of O_2 by electrons. These radical species oxidize the degraded Sodium Dodecyl Sulfate compound on the surface of the Ag_3PO_4 photocatalytic material of red banyan fruit extract to form simpler compounds to reduce its concentration.

Table 2. Relationship between C/C_0 to the visible irradiation time

Time	SDS 0,4 mg.L^{-1}		
	C_0	C	C/C_0
0	0.4	0.4	1
30	0.4	0.28	0.7
60	0.4	0.23	0.57
90	0.4	0.17	0.42
120	0.4	0.08	0.2
150	0.4	0.08	0.2
180	0.4	0.08	0.2

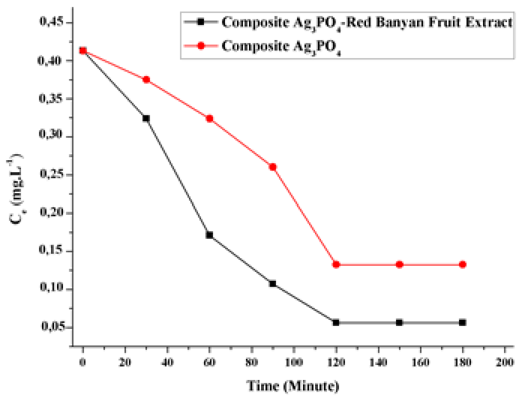

Figure 6. Graphic of the relationship between final concentration and time of visible light irradiation time

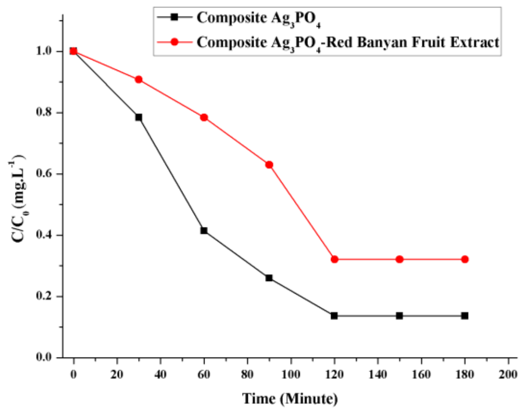

Figure 7. Graph of the relationship between C/C_0 against the time of visible light irradiation

The optimum time is one of the important parameters to determine the most significant decrease in SDS concentration. The reaction rate of hydroxyl formation is influenced by the irradiation time of the degradation process. This relationship is directly proportional, where the longer the irradiation time, the more hydroxyl radicals are formed. Hence, the efficiency of degradation is increasing over time.

In order to determine the effect of time on SDS concentration, the photodegradation was performed in these time varitions; 30, 60, 90, 120, 150 and 180 minutes. The results of testing the effect of irradiation time on photodegradation of sodium dodecyl sulfate solution and their comparison with Ag_3PO_4 are shown in Figures 6 and 7.

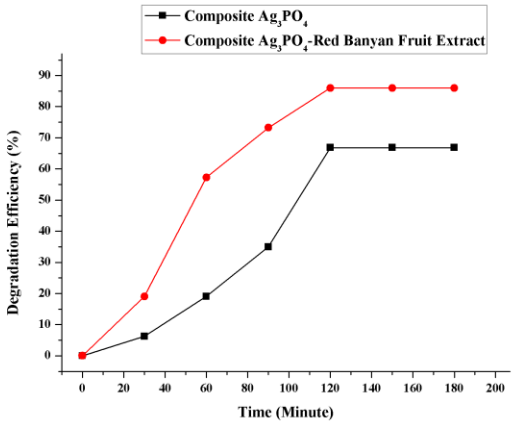

Figure 8. Efficiency profile of SDS degradation against irradiation time

The efficiency of SDS degradation over time is shown in Figure 8. Based on these graph it can be seen that the irradiation time of visible light influences SDS degradation. Where the degradation efficiency of NaDS is directly proportional to the increase in contact time between silver phosphate composites (Ag_3PO_4)-red banyan fruit extracts against SDS. The optimum time obtained from the contact time between silver phosphate composites (Ag_3PO_4) - red banyan fruit extract with SDS is 120 minutes with maximum degradation efficiency by Ag_3PO_4 silver phosphate composite red banyan fruit extract reaching 85.9%.

4. CONCLUSION

Based on the above discussion, it can be concluded that the silver phosphate composite (Ag_3PO_4)-red banyan fruit extract can be used as an ingredient in the handling of detergent waste in a more efficient aquatic environment with degradation obtained by 85.9% at the optimum contact time of 120 minutes for a concentration of 0.4 ppm, compared with 66.8% Ag_3PO_4 photocatalytic activity under visible light irradiation.

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