



Ability of Water Lettuce (*Pistia stratiotes*) And Water Hyacinth (*Eichhornia crassipes*) To Remove Methylene Blue Anionic Surfactant (MBAS) From Detergent Wastewater

N. Hendrasarie*[†]  and C. Redina*

*Department of Environmental Engineering, University of Pembangunan Nasional “Veteran” Jawa Timur, Indonesia

[†]Corresponding author: N. Hendrasarie; novirina@upnjatim.ac.id

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ABSTRACT

ABS was the first surfactant used in detergent formulations, but because its molecular structure is branched, it is difficult to decompose biologically, making ABS a toxic compound for the environment. This study aims to remove MBAS surfactant, using a combination of phytoremediation and filtration methods to remove surfactant (MBAS) Chemical Oxygen Demand (COD) from detergent wastewater by optimizing operating factors such as pH, contact time, plant type, and filter media. Water lettuce (*Pistia stratiotes*) and water hyacinth (*Eichhornia crassipes*) were selected as plant species and silica-activated carbon was used as filter media. Water lettuce and hyacinth were grown in a 10-liter reactor with detergent wastewater samples for 6 and 12 days. Filter media are placed in the reactor in use, and aeration is done. The efficiency for reducing COD was 81.73%, and the efficiency for surfactant was 99.42% for each experiment, which was thought to be because of plant adsorption and filtering processes. The water lettuce (*Pistia stratiotes*) plant had the maximum adsorption capability for all the qualities evaluated, with a surfactant content in the roots of 27543.24 (mg/kg MBAS), compared to the water hyacinth plant, which only absorbed 2597.95 (mg/kg MBAS).

INTRODUCTION

Detergent is the highest pollutant in the water, along with world detergent production, which reached 2.7 million t.y⁻¹ with an increase of 5% annually. The active substance in this waste needed to be noticed because it could be a threat to the health and environment. Detergent wastewater is usually produced from washing and laundry waste and has a main content in the form of surfactant and builder in phosphate form. The waste continued to increase as the community grew. Most of the detergent wastewater is directly discharged into the water bodies without going through a treatment or appropriate process. This could lead to environmental damage (Suwandhi et al. 2022, Moondra et al. 2021, Saini et al. 2021).

People have less understanding of the adverse effects of detergent waste when it is directly discharged into the environment. This resulted in disturbance to the environment, even the community itself. The other environmental impact caused by detergent waste was also eutrophication in the waters. Aquatic plants consume oxygen in the water to decrease dissolved oxygen content and disrupt the lives of

other aquatic biota, such as fish and benthic invertebrates. Surfactants in detergent waste may harm humans, particularly with direct contact with the skin, and cause dryness, blister, easily peeled skin, allergies, and itch (Rebello et al. 2014, Simoni et al. 1996).

Detergent is a widely used surfactant. Detergent is used for both household and industrial purposes. The anionic type surfactant in the form of sulfonate (SO₃) is the most widely used to produce detergent surfactants. The detergent class of sulfonates is divided into two types: branched chain types such as Alkyl benzene sulfonate (ABS) and straight-chain types such as Linear Alkylbenzene sulfonate (LAS) (Al Idrus et al. 2020, Correa dos Santos et al. 2022).

ABS was the first surfactant used in detergent formulations, but because of its branched molecular structure (Fig. 1), ABS is a toxic compound to the environment. Linear alkylbenzene sulfonate (LAS) is widely used to replace branch alkylbenzene sulfonate (ABS) in large quantities around the world because it is a detergent material with a straight molecular structure (Fig. 1) and is more biodegradable than ABS. (Lee 2013, Lundholm 2013, Parde

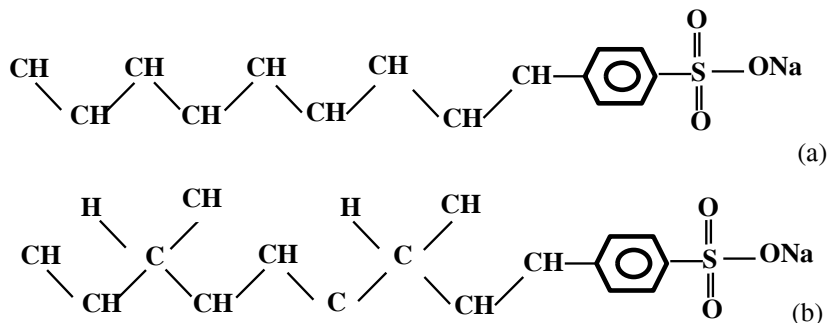


Fig. 1: Straight Chain and Branched Chain Detergent Molecule Structure.

et al. 2021). LAS can reduce surface tension and emulsify fat, making it useful as a fat solvent and for protein denaturation (Hudori & Soewondo 2009). LAS slows the diffusion of oxygen from the air into the waters, lowering dissolved oxygen (DO) (Suastuti et al. 2015).

In addition, the surfactant may cause slowing oxygen diffusion from the air to the water and lead to the reduction of dissolved oxygen (DO) in the water (Hendrasarie et al. 2021, Kataki et al. 2021).

Chemical Oxygen Demand (COD) is a benchmark for water pollution by organic substances, which could be naturally oxidized by microorganisms and cause depletion of dissolved oxygen in the water. Some organic materials in water are resistant to biodegradation. However, they would be degraded chemically through oxidation. There are several methods for treating detergent waste. Based on research, existing methods are the photocatalytic method of UV light, bio-sand filter (An & Verhoeve 2019), and activated carbon (Hendrasarie et al. 2021). One method that could be applied in treating this detergent waste is phytoremediation. Phytoremediation has been proven to reduce surfactant content in detergent waste (Fitrihidajati et al. 2022, Kettenring & Tarsa 2020). Water lettuce and hyacinth could be used as hyperaccumulator plants to treat laundry waste (Cooper 2005, Dong et al. 2005).

Phytoremediation is a technology that involves plants in the remediation processes. Some plants can absorb, transform, and degrade pollutants in waste (Heidari 2003, Hu et al. 2014). Plants used in the phytoremediation process are also called hyperaccumulator plants. Hyperaccumulator plants include water lettuce, water hyacinth, sunflower, bamboo, water kale, and others. Some types of aquatic plants can process organic or inorganic compounds in wastewater. Aquatic plants also have a group of microbes called rhizobacteria that surround the plant. This type of bacteria also can decompose organic and inorganic substances (Grime

1998, Khan & Bano 2016). Adding aeration will fulfill the oxygen demand for microbes found in plant roots and enhance the decomposing process of organic and inorganic substances.

Water lettuce is a common hyperaccumulator plant used for phytoremediation. This plant can treat heavy metals and inorganic and organic waste. This plant can be found floating in swamps or ponds. Known as a pond's protective plant, water lettuce is a monocot plant with thick leaves and strings like roses. The leaves could reach 14 cm and had no stems. The roots have long hair and are surrounded by air bubbles that increase the buoyancy of the plant (Knox et al. 2008, Shahid et al. 2018). Water hyacinth is a type of floated plant freely on the surface of the water and has dark green leaves attached to the spongy stems. The root has branches (fibers) in water and is dark in color. Water hyacinth is easy to grow and can cover all large water surfaces in a very short time. This plant is also widely used in phytoremediation to treat livestock, sugar mills, paper, and palm oil waste.

Filtration is a process of separating water and particles that are not settled during sedimentation and through porous media. Most media often used in filtration are sand, activated carbon, anthracite, and coconut shells. Filtration is divided into two types: rapid sand filter and slow sand filter. A rapid sand filter is often used for drinking water treatment. Types of this sand media are divided into two, namely single-media in the form of sand and multi-media, which consists of 2 media or more. Sand filter media could reduce pollutant content with effectiveness between 18-75% (Mohd Saad et al. 2021, Wang et al. 2019).

The process that occurred in the filtration could not be separated from the biological process that involved microorganisms. These microorganisms are found around the filter media and from wastewater itself, then will be accumulated in the filter media and transformed into biofilms. Biofilms may grow well due to their activity that

utilizes organic substances and converts organic compounds into simpler compounds, such as water, carbon dioxide, and biomass. In addition, biofilm may reduce the concentration of organic materials in the waste by lowering the concentration of organic wastewater (Sayadi et al. 2012, Rahman et al. 2020).

The main object of this study was to evaluate the ability of water lettuce and water hyacinth to decline the surfactant and COD concentration in detergent wastewater. The combined treatment of phytoremediation and filtration was used to enhance the remediation processes. In addition, the morphological parameters of the plant were also measured as a response to detergent wastewater exposure.

MATERIALS AND METHODS

Water lettuce and water hyacinth were collected from a local pond in Surabaya City. The plants were transported to the laboratory for an acclimatization process in a 10 L tank for 7 days. The filter media used in this experiment were sand, silica sand, and active carbon. Detergent wastewater was collected from the drainage near densely populated areas and measured the water quality parameters (Table 1). The experiment was a laboratory scale, with a 1:10 scale comparison with the reactor's size of 26 × 26 × 30 cm. The water level above the media was 9 cm.

The phytoremediation and filtration were conducted in the same reactor. The reactor consists of a plant and two-combined filter media with 3 cm for each filter media (Table 2). The control reactors were used with two-combined filter media only and without plants. The residence time was 6 days and 12 days, and the parameters used for removal were surfactant and COD. The pH and temperature were also measured during the experiment.

The morphological parameters measured in this experiment were plant height (cm), root length (cm), the number of leaves, leaf surface area (cm²), and the number of new branches. Data on existing plant conditions were

Table 1: Water quality parameter of detergent wastewater.

Parameter	Value
BOD ₅ [mg.L ⁻¹]	1268
COD [mg.L ⁻¹]	2884
TSS [mg.L ⁻¹]	616
Oil & Grease [mg.L ⁻¹]	64.00
Surfactant (MBAS) [mg.L ⁻¹]	734.86
Phosphate [mg.L ⁻¹]	249.42
pH	9.50

Table 2: The combination of a reactor for phytoremediation and filtration.

Duration	Filter Media	Plant
6 days	Sand-Active carbon	Water lettuce
		Water hyacinth
12 days	Sand-Silica sand	Water lettuce
		Water hyacinth
	Sand-Active carbon	Water lettuce
		Water hyacinth
Sand-Silica sand	Water lettuce	
	Water hyacinth	

presented in graphical form of the average value of plant parts. The total plants used in this study were 16 water lettuce and 16 water hyacinths. At the time of the treatment, 16 plants would be divided into two parts, based on the variation in their 2-residence time, and then the average value of 8 plants was used.

RESULTS AND DISCUSSION

Surfactant and COD Removal

In general, using water lettuce and water hyacinth and a combination of media filters can reduce the concentration of surfactants in the range of 98-99%. The Highest percentage of the surfactant decreased was 99.42% in water hyacinth in combination with sand-active carbon for 6 days. Meanwhile, the lowest percentage of surfactant removal was 98.88% in water lettuce with sand-active carbon for 6 days. The decrease in surfactants in water can occur due to absorption by plants through the roots, which will then be transported to the plant's organs. In addition to the absorption mechanism, the existence of microorganisms that are usually in plant roots can also play a role in degrading organic compounds such as surfactants. Microorganisms that could help to decompose surfactants were rhizobacteria from the genus of *Pseudomonas* (Zhang et al. 2016, Yu et al. 2021). The surfactant breakdown by microorganisms was divided into three stages. First was the oxidation of the alkyl group at the end of the LAS chain, forming an intermediate in the form of alcohol. The process would occur until the chain had only 4-5 carbon atoms (Masoudian et al. 2020). Next, through the desulfonation stage, the sulfonate group was removed and catalyzed by a complex enzyme, NAD(P)H coenzyme, and oxygen formed phenolic hydroxides in the benzene ring. Then the final stage was the opening of the benzene ring through the meta or ortho pathway (Scholz et al. 2007, Wiegleb et al. 2017).

The result of COD Removal in Fig. 2 showed sand-active carbon for 12 days has the highest percentage, 81.73% in

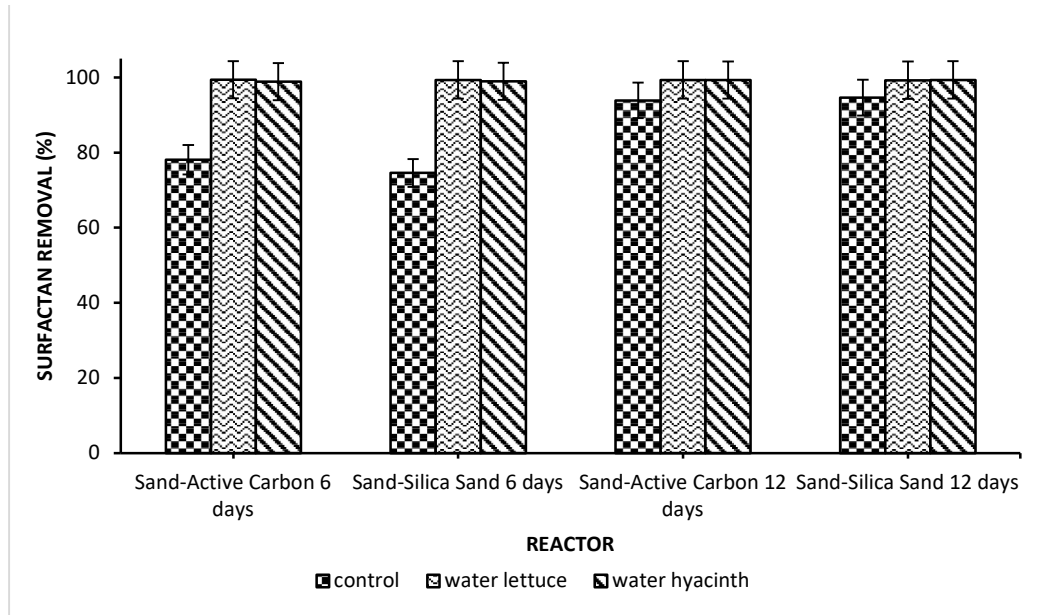


Fig. 1: Surfactant removal using plants and filter media.

water lettuce and 78.67% in water hyacinth. In addition to the degradation process of organic material by plants, the filtration process that uses sand-active carbon can increase the decrease in COD during treatment. The use of aeration intended to increase the aeration of oxygen in wastewater can help the existence of microorganisms in the roots of plants and microorganisms in the filter layer in the decomposition process. The use of slow sand filters was usually due to the

more optimum ability to remove organic materials (Scott et al. 2020). Besides, the contact time of wastewater with the media was longer. The longer the contact time, the more perfect the role of microorganisms in degrading organic material (Cong et al. 2021, Al-Idrus et al. 2020). A slow sand filter could be applied considering the time when the wastewater comes into contact with the filter media, drainage discharge, and filtration speed.

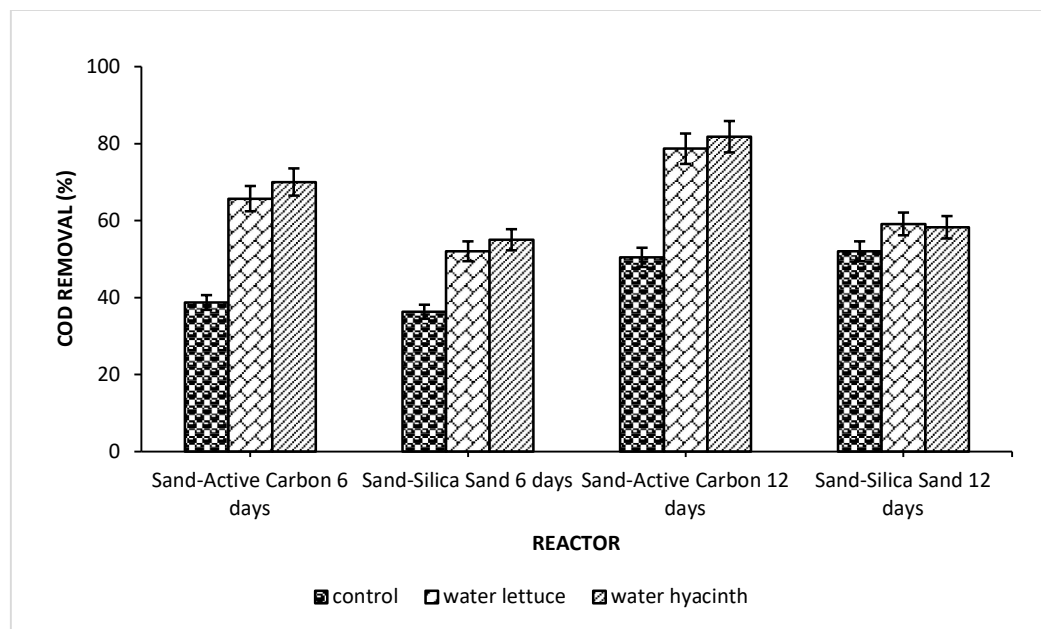


Fig. 2: COD removal using plants and filter media.

Anova One-Way statistical tests were performed to determine the relation between factorial value (residence time) toward the responses (percent of surfactant removal and COD). The test was carried out using a trust level of 95%. The Influence of residence time on surfactants and COD resulted in a P-value of 0.00 (P-value <0.05). This showed a relationship between the percentage decrease and residence time.

Plants' Response to Surfactant Exposure

The morphometric parameter shown first was the average plant height in Fig. 3. In the acclimatization stage, all parts of the plant grew normally. This could indicate that the plants had been acclimatized well for 7 days. After acclimatization, the average height of water hyacinth was 28-35.4 cm, and water lettuce was 16.2-18.8 cm at the initial stage of the experiment.

After 6 days' residence time, the plant's height of both plants experienced a decrease. At the second treatment with a residence time of 12 days, both plants showed a decrease in height from day 1 to day 6. Meanwhile, from day 7 to day 12, the plants' condition slightly improved. From day 1 until day 6, the plants may carry out maximum absorption and adapt to the new environment floating on the wastewater. From day 7 until day 12, the average height of the plants started to increase, which means the plants had been able to adapt and survive in wastewater.

The number of leaves in the initial experiment in water lettuce was 8.88-9.25 cm, and water hyacinth was 8-8.25 cm (Fig. 4). At 6 days' residence time, the number of leaves at both plants decreased. Whereas at 12 days' residence time, both plants showed a similar pattern. The average number of leaves in both plants gradually decreased until day 4 and day 5. However, water lettuce showed an increase in leaves until day 12. In contrast, the water hyacinth continued the decrease until day 10, then turned into arising until day 12 in Fig. 4. The changes of both plants to the circumstances also could be observed from the number of leaves. The first 6-day stage was the adaptation period, and the plants would experience physiological stress from the wastewater, which might be absorbed. After that period could be passed, the plants would continue to grow with the adapted condition. Leaves are an important part of plants, particularly for photosynthesis. Exposure to surfactants may change the enzyme for metabolism and cause chlorosis (Hu et al. 2014, Masoudian et al. 2020).

The root length of both plants showed a noticeable decrease at the 6 days of residence time. Meanwhile, at 12 days of residence time, both plants showed a slight decrease until day 6 and continued to grow until day 12 (Fig. 5). In aquatic plants, the root is essential, particularly to absorb nutrients. Moreover, in the polluted media exposed to wastewater, the root would be the first part that interacts directly with the pollutants. Therefore, the effect

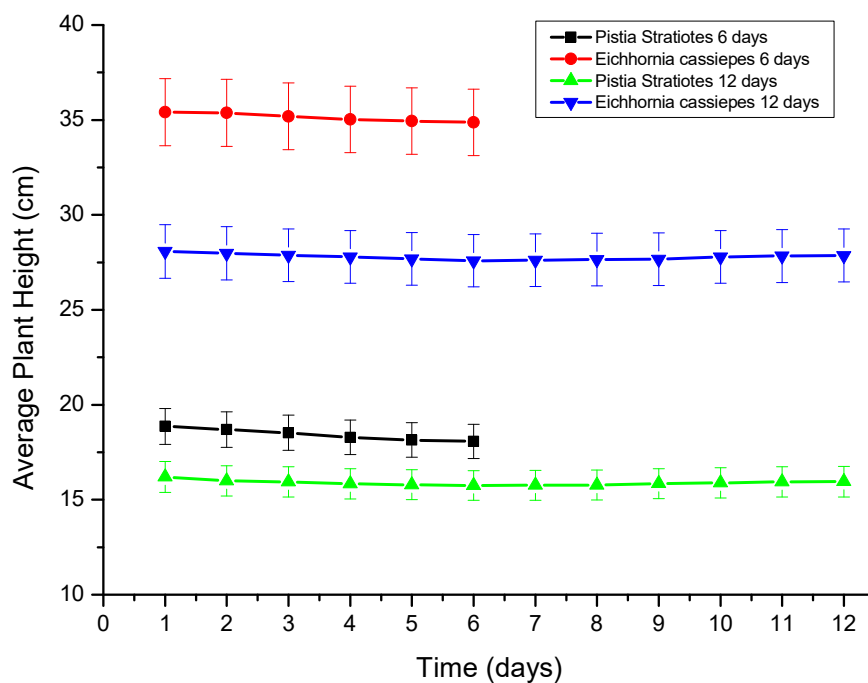


Fig. 3: Plant height of water lettuce and water hyacinth.

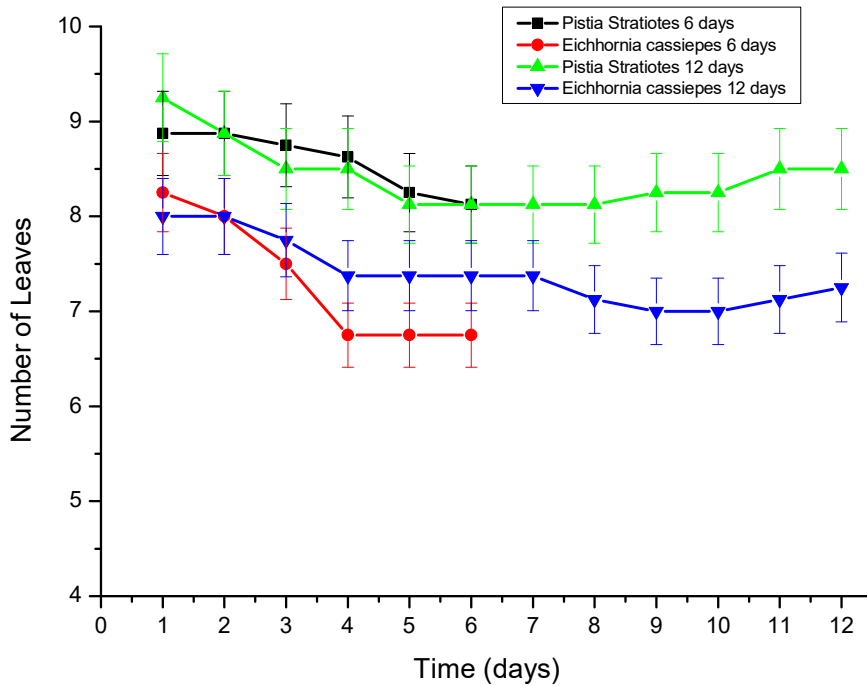


Fig. 4: The number of leaves of water lettuce and water hyacinth.

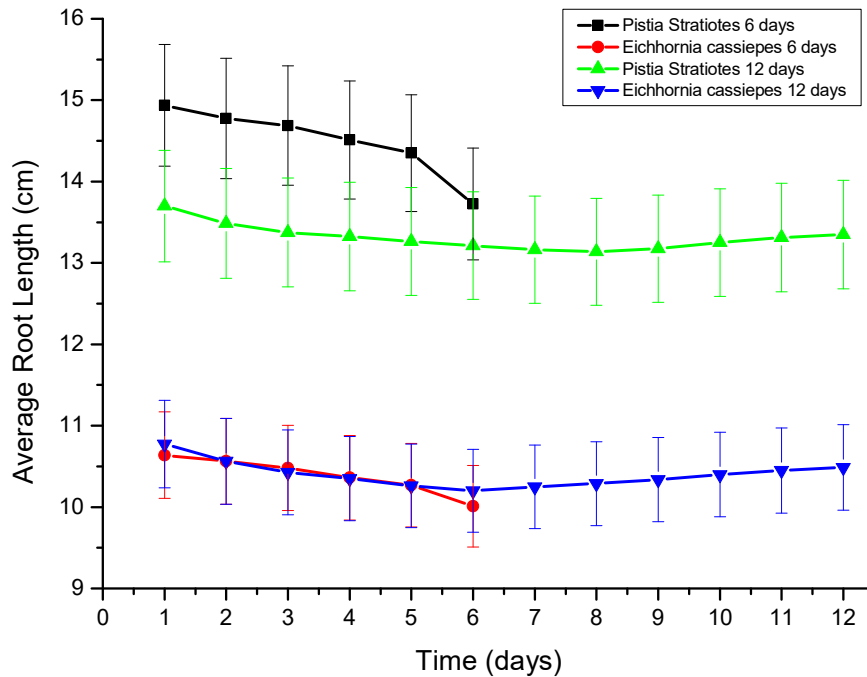


Fig. 5: Average root length of water lettuce and water hyacinth.

of wastewater could be responded to the changes in the root length. In certain conditions, the plant would be able to adjust to stress conditions and survive (Shahid et al. 2018).

A similar result also occurred in the leaf surface area. During 6 days of exposure to wastewater, as can be seen from Fig. 6, both plants showed a decrease in leaf surface

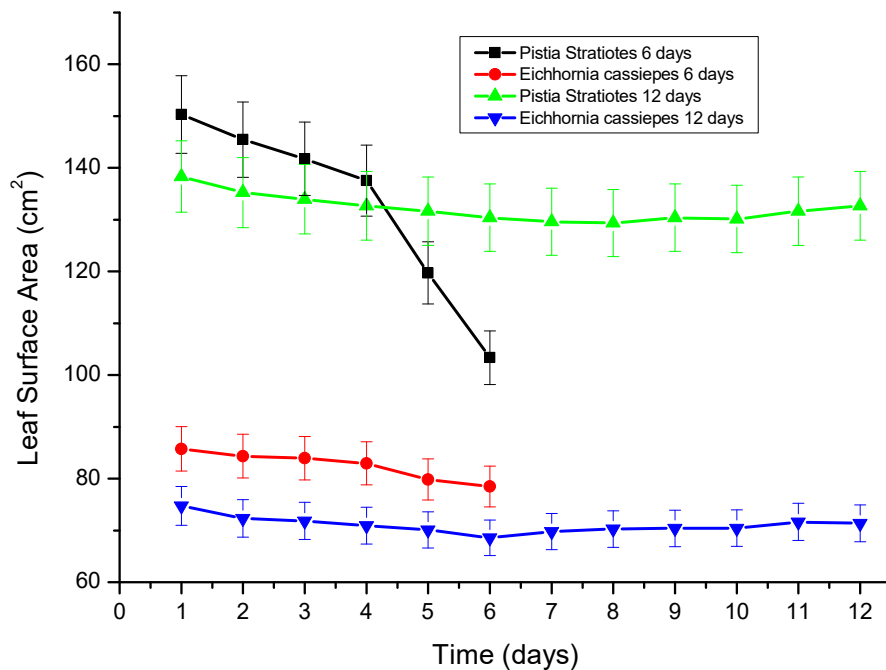


Fig. 6: Leaf surface area of water lettuce and water hyacinth.

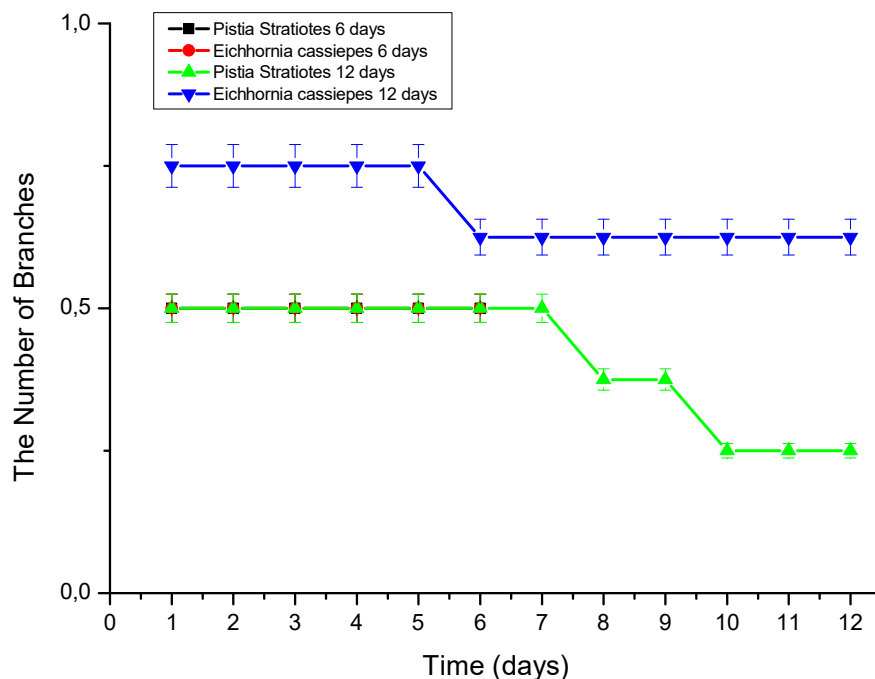


Fig. 7: The number of branches of water lettuce and water hyacinth.

area. However, water lettuce showed a considerable decrease on the last day. At 12 days of residence time, water hyacinth and water lettuce showed a moderate change in response to wastewater exposure. Based on the result, a significant

decrease in the leaf surface area of water lettuce at day 6 might be attributed to the morphological factors, in which the leaf's position is relatively lower and has no stems. Therefore, the leaves were exposed directly to the wastewater

(Hasan et al. 2021, Correa dos Santos et al. 2022). Unlike water hyacinth, which has stems, it could keep the leaves from direct contact with wastewater.

The result of 6 days of residence time is shown in Fig. 7. Both plants had no additional branches. Meanwhile, at 12 days of residence time, both plants' branches decreased. Water hyacinth showed numerous decreases compared to water lettuce during the exposure. The plants also experienced symptoms such as yellowing of leaves, withered leaves, and shortened roots. The growth of new branches in poor conditions was difficult for plants. Mostly, the plants were attempting to adapt and survive in poor conditions. Some plants would survive and tend to meet their basic growth. In addition, growing new branches indicates that plants can adapt and survive without any environmental disturbance (Knox et al. 2008).

Surfactant Accumulation in Plants

The existence of surfactant in plants, shown in Table 3, indicates the plants were able to absorb and keep in the organ. As the photo process mechanism in plants, surfactant would be degraded and result from the lower concentration. In general, the concentration of surfactant in both plants at 6 days was greater than 12 days of residence time. Water lettuce and water hyacinth absorb a high amount of surfactant from the wastewater at the initial treatment. This was the mechanism of adaptation for the plants by adjusting to the new environment (Linh et al. 2021, Al-Idrus et al. 2020). Surfactants in plant tissues had not been completely transformed into simple forms which would be released into the air through the leaves. The surfactant concentration in 12 days' residence time was less than 6 days because the plants had done the process of phytovolatilization. This process changed the surfactant substances to a simpler form and then was released into the air through leaves tissue. Microorganisms also assisted the decrease in surfactant substances in the root. The longer microorganisms treat the waste, the more maximum and effective decomposition of surfactant substances.

The Influence of pH and Temperature on Plants

The pH of wastewater during the experiment ranged from 7.6 to 8.4. Water hyacinth could grow and develop well at pH 6-8 (Zhang et al. 2016). At first, the waste in the reactor had a pH above 8, causing the growth of water hyacinth plants to decrease. After a few days, the pH of the wastewater in the reactor decreased. Therefore, the plant turned to show increased growth. The lower pH would cause toxicity for the plants with a minimum threshold of pH 4.2. Moreover, if the plant lives in a toxic environment, it would cause a high death

Table 3: Surfactant the plant's parts (6 days and 12 days).

Plants	Plant parts	Surfactant [mg.kg ⁻¹] LAS)	
		6 days	12 days
Water hyacinth	Roots	2597.95	164.11
	Stems	178.48	110.49
	Leaves	134.09	148.58
Water lettuce	Roots	27543.24	248.41
	Leaves	3158.92	126.61

probability for the plants (Hendrasarie et al. 2021, Ratnani et al. 2013). The results showed that the P-value of pH against COD and surfactant was greater than 0.05 (P-value > 0.05), meaning there was no relationship between pH and the test parameters of both surfactants and COD.

The temperature of wastewater in growth media for water hyacinth and water lettuce during the study ranged from 25-29°C. The temperature needed for plants to grow and develop properly was at a temperature of 20-30°C (Hendrasarie & Dieta 2019, Katakai et al. 2021).

The temperature at the time of the study was still in the range for plants to grow well. Therefore, both plants could survive until the end of the study, even though the morphological condition of the plants had decreased due to the accumulation of waste. The results showed that the temperature P-value toward COD and surfactants was greater than 0.05 (P-value > 0.05), meaning there was no relation between temperature and the test parameters of both surfactants and COD.

CONCLUSION

The results of this study show that a combination of phytoremediation and filtration can effectively decompose the MBAS surfactants and COD found in detergent wastewater. With an aeration rate of 14 L/minute, a combination of the water lettuce (*Pistia stratiotes*) plant and activated carbon was able to remove 99.42% of MBAS surfactant for 6 days, meanwhile reducing COD for 12 days and achieve a reduction of 81.73%. The state of plants, plants started adjusting to their surroundings on the eighth day, especially the water lettuce and water hyacinth plants.

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ORCID DETAILS OF THE AUTHORS

Arpita Ghosh: <https://orcid.org/0000-0002-7651-1558>