Synthesis of Chitosan-Alginate Beads and Its Application for Alkyl Benzene Sulfonates (ABS) Adsorption

N P S Ayuni*, I N Sukarta and P A Wulandari

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Pendidikan Ganesha, Indonesia.

*Corresponding author: sri.ayuni@undiksha.ac.id

Abstract. ABS is the largest group of anionic surfactants. Anionic surfactants (AS), especially ABS are used extensively due to their impacts on ecosystems and are usually disposed of after their use in the environment. Therefore, they represent one of the main causes of water pollution. Methods have been proposed to remove surfactants such as adsorption with beads. This study aims to analyze the results of the synthesis and characterization of chitosan-alginate beads and determine the efficiency adsorption of ABS. The synthesized beads were characterized by swelling tests. To find out the maximum efficiency of ABS, ABS adsorption with chitosan-alginate beads was carried out by varying pH (5, 6, 7, 8, and 9), time (15, 30, 45, 60, 75, and 90 minutes) and ABS concentration (10, 20, 30, 40, and 50 mg/L). The results of the adsorption solution were measured by a UV-Vis spectrophotometer. The results of the swelling test on beads for 24 hours reached an average of 148.18%. The maximum efficiency adsorption of chitosan alginate beads was determined to be 46.46% with an initial ABS concentration of 30 mg/L at pH 6 in 60 minutes.

1. Introduction
Surfactants are a diverse group of chemicals with cleaning properties and consist of two heads with a different polarity or solubility in water: a polar head group, which is well solvated in water, and a non-polar hydrocarbon tail, which is not easy to dissolve in water. Surfactants combine hydrophobic and hydrophilic properties in one molecule. Synthetic surfactants are economically important chemicals. They are widely used in household cleaning detergents, personal care products, textiles, paints, polymers, pesticide formulations, pharmaceuticals, mining, oil recovery, and pulp and paper industries. The world production of synthetic surfactants amounts to 7.2 million tons annually [1,2].

Surfactants are classified by their ionic activity in water into four types: anionic, cationic, non-anionic, and amphoteric [3]. ABS is the largest group of anionic surfactants. Anionic surfactants (AS), especially ABS are used extensively due to their impacts on ecosystems and are usually disposed of after their use in the environment [4,5]. Although a wide range of physical and chemical processes such as chemical precipitation, ion exchange, membrane filtration, solvent extraction, etc. are available for the removal of surfactants; most of these methods are not practicable. Therefore, the development of low-cost methods to remove surfactants has received the attention of scientists worldwide and biosorption has been recognized as a cost-effective method of removal of surfactants contaminants in water using low cost bioadsorbents such as activated carbons, burned brick particles, clay, some aquatic weeds, agricultural and biological wastes, chitosan, and zeolites, etc. Chitosan is...
the second abundant polycationic biopolymer after cellulose derived from chitin. Chitosan is insoluble in air, but it is a repetitive structure of the amine group that allows it to be dissolved in dilute acids. Under acidic conditions, amine groups can easily be protonated and become positively charged. In this experiment, chitosan was free with alginate. Combining chitosan with alginate which is formed into chitosan-alginate beads is an effective way to achieve ABS levels in laundry waste. Chitosan-alginate in the form of beads has a larger pore size, better diffusion properties, and is hydrodynamic thereby increasing the adsorption ability. The present study aims to obtain a characterization of chitosan alginate beads and determine the efficiency adsorption of ABS.

2. Materials and Method

The materials used were distilled water, chloroform, methylene blue, chitosan, alginate, acetic acid 5% solution, sodium hydroxide solution, ABS, sulfuric acid 6 N, sodium dihydrogen phosphate monohydrate, and isopropyl alcohol. The instruments used in this research are UV-Vis spectrophotometer, analytical balance, magnetic stirrer, and glassware.

2.1 Synthesis Chitosan-Alginate Beads

The chitosan solution is made by dissolving 1 gram of chitosan in an acetic acid solution 5% of 90 mL in a 500 mL beaker [6]. Then the alginate solution is made by dissolving 0.1 gram in 10 mL of distilled water [7]. The chitosan solution and alginate solution are then mixed and stirred until homogeneous. This solution is then stirred with a stirrer for 24 hours. The mixture of chitosan alginate solution is then printed using a dropper by dropping in NaOH 2 M solution and soaking for 3 hours. The chitosan alginate beads formed were filtered. After that, the beads are washed with distilled water until the beads are neutral. Chitosan alginate beads are then dried using an oven at 50 °C for 2 hours [8].

2.2. Determination of pH, Contact Time, and Optimum ABS Solution Concentration

The 0.1 grams of chitosan-alginate beads were added to 15 mL of 30 mg/L ABS solution with varying pH (5, 6, 7, 8, and 9), then stirred for 60 minutes at 150 rpm [9]. The filtrate obtained was extracted by the MBAS procedure. Then the optimum contact time was determined with variations (15, 30, 45, 60, 75, and 90 minutes) with the adsorbent mass of 0.1 gram in 15 mL of 30 mg/L ABS solution at the optimum pH. The filtrate obtained was extracted by the MBAS procedure (5 mL of the filtrate was taken and put into a 50 mL volumetric flask, then added 10 mL of 100 mg/L methylene blue solution and distilled water until the limit mark. The mixture of this solution was extracted with 10 mL of chloroform. The organic phase (the resulting chloroform) was measured for its absorbance value using a UV-Vis spectrophotometer at a wavelength of 652 nm). pH and contact time that produce maximum adsorption efficiency are used to determine the optimum concentration of ABS solution (10, 20, 30, 40, and 50 mg/L) [8].

2.3 Data Analysis

The results of the synthesis of chitosan-alginate beads were then characterized. The results of characterization include the water adsorption test (swelling test) (Equation1). The data will be analyzed descriptively. ABS adsorption efficiency data using a UV-Vis spectrophotometer will be analyzed quantitatively with the results obtained are absorbance data and ABS concentration. From these data it can be calculated the ABS adsorbed concentration and the efficiency (%E) of the variation in contact time and ABS concentration. The maximum adsorption efficiency of ABS with variations in pH, variations in contact time, and ABS concentration was calculated using Equation 2. The values obtained from these data will be presented in graphical form and analyzed descriptively.
\[
\text{% Swelling Test} = \left( \frac{W_{\text{wet}}-W_{\text{dry}}}{W_{\text{dry}}} \right) \times 100\% 
\] (1)

\[
\text{%E} = \frac{C_o-C_s}{C_o} \times 100\% 
\] (2)

\(C_o\) was the initial concentration (mg/L), \(C_s\) was the residual concentration (mg/L)

3. Results and Discussion

Alginate beads with a mass ratio of chitosan and sodium alginate of 0.1: 0.01 (g /g) and a volume ratio of acetic acid and distilled water 9:1 (v/v). Beads were synthesized from chitosan stirring in acetic acid solution 5\% and alginate in distilled water. The results of chitosan alginate beads show in Figure 1.

In an acidic atmosphere, chitosan forms polycationic, while alginate forms polyanionic. Polycationics and polyanionic will react to form polyelectrolyte through ionic reactions [10]. The chitosan material modified with alginate aims to increase the active group. When chitosan and alginate are combined into one, there will be a reaction between the carboxyl group of the alginate and the amine group from chitosan to form an amide group so that it can increase the adsorption ability [11]. To determine the interaction between the carboxyl group and the amine group of these two materials
The swelling test was carried out to determine the capacity of the beads to absorb water (hydrophilic nature) so that they were able to expanded due to the presence of pores between polymer bonds [8]. Water absorption was carried out using the gravimetric method, namely by calculating the difference between the dry weight and the wet weight of the beads. From the research results, the swelling test on beads for 24 hours reached an average of 148.18% (Table 1). These results indicate that the chitosan-alginate beads can expand in water so that it can be used as an adsorbent [8]. When a biopolymer comes into contact with a liquid, there will be expansion due to thermodynamics. When the beads expand, the mobility of the polymer chain increases so that the penetration of the solvent is easier. The development of chitosan-alginate beads is due to the ionic interaction between the amino group (NH$_3^+$) of chitosan and the carboxyl group (COO$^-$) of the alginate. Chitosan-alginate beads have a large degree of swelling which indicates that they are good at absorbing water. The amount of water that can be absorbed in the beads is due to the pores of the beads. The swelling test of the beads can show the hydrophilicity of the beads. The more chitosan composition will increase the hydrophilicity of the beads so that the number of diffused ABS molecules will increase.

Table 1. Swelling Test of Chitosan-Alginate Beads

| Replication | $W_{\text{wet}}$ (g) | $W_{\text{dry}}$ (g) | %    |
|-------------|---------------------|---------------------|------|
| 1           | 0.1012              | 0.2518              | 148.81|
| 2           | 0.1004              | 0.2483              | 147.31|
| 3           | 0.1035              | 0.2571              | 148.41|
| **Average** |                     |                     | **148.18** |

Figure 3 shows that the adsorption of ABS by chitosan-alginate beads shows an optimum pH efficiency at pH 6 with an efficiency of 48.25%. The decreasing of the acidity of the food solution will increase the protonation by neutralizing the negative charge from the adsorbent surface so that it will facilitate the diffusion process in the adsorbent area. When the beads adsorption process which has the main NH$_2$ group will undergo a protonation process to form NH$_3^+$ so that there will be adsorption of solution cations by the beads through the exchange of H$^+$ ions which occur electrostatically. In this study, the pH 6 beads reached the optimum condition because the NH$_2$ group is in the form of NH$_3^+$ so that it acts as an electron-pair donor that produces complex compounds. pH above 6, there is a decrease in adsorption efficiency because pH above 6 contains a lot of OH$^-$ ions, which results in a rejecting reaction with the adsorbent, and precipitation will occur so that the absorption capacity is reduced.

![Figure 3. The Adsorption of ABS by Chitosan-Alginate Beads with pH Variation](image)
Figure 4 shows that the chitosan-alginate beads can adsorb optimally in 60 minutes with an efficiency value of 68.16%. At the contact time of 15, 30, and 45 minutes there is still a space that has not been filled by the ABS contained in the beads because the active groups in the beads have not interacted optimally. In the 60th minute the space in the adsorbent is filled optimally, this is because the longer the contact time, the more likely the adsorbed substance will be absorbed. Meanwhile, at the contact time of 75 and 90 minutes, there was a decrease in adsorption ability, with increasing contact time, the absorption of the beads would decrease so that the beads were unable to bind the ABS molecules, and the ABS molecules as adsorbate would be released from the beads.

![Figure 4. The Adsorption of ABS by Chitosan Alginate Beads with Time Contact Variation](image)

Figure 5 shows that the optimum concentration efficiency is at a concentration of 30 mg/L with an adsorption efficiency value of 46.46%, in this state the empty spaces on the adsorbent have been filled optimally by ABS because the active groups of the beads bind to ABS. Concentrations of 10 and 20 mg/L have lower adsorption efficiency values because of the large number of empty spaces in the adsorbent that have not been filled by ABS. At concentrations of 40 and 50 mg/L, there was a decrease in the value of adsorption efficiency because the concentration was too high which caused the amount of ABS in the solution to be not proportional to the number of adsorbents so that the absorption decreased. The addition of ABS concentration will decrease the adsorbent absorption because in this condition the adsorbent is saturated. The concentration of ABS is closely related to the number of active sites of the adsorbent, if the number of active sites on the adsorbent surface is large enough compared to the amount of ABS, the absorption efficiency will be high.

![Figure 5. The Adsorption of ABS by Chitosan-Alginate Beads with Concentration Variation](image)
4. Conclusions

The results of the swelling test on beads for 24 hours reached an average of 148.18%. The maximum efficiency adsorption of chitosan alginate beads was determined to be 46.46% with an initial ABS concentration of 30 mg/L at pH 6 in 60 minutes.

Acknowledgments

This work was supported by Research and Community Service Institution Universitas Pendidikan Ganesha under Penelitian Terapan Scheme 2020 (contract number: 793/UN48.16/LT/2020).

References

[1] Ying G G 2006 Fate, behavior and effects of surfactants and their degradation products in the environment Environment international 32 (3) 417-431
[2] Mungray A K and Kumar P 2009 Fate of linear alkylbenzene sulfonates in the environment: a review International Biodeterioration & Biodegradation 63 (8) 981-987
[3] Ghoochani M, Shekoohiyan S, Mahvi A H, Haibati B and Norouzi M 2011 Determination of detergent in Tehran ground and surface water American-Eurasian J Agric Environ Sci 10 (3) 464-469
[4] Verge C, Moreno A, Bravo J and Berna J L 2001 Influence of water hardness on the bioavailability and toxicity of linear alkylbenzene sulphonate (LAS) Chemosphere 44 (8) 1749-1757
[5] Brandt K K, Hesselso M, Roslev P, Henriksen K and So J 2001 Toxic effects of linear alkylbenzene sulfonate on metabolic activity, growth rate, and microcolony formation of Nitrosomonas and nitrosospira strains Applied and environmental microbiology 67 (6) 2489-2498
[6] Nitsae M, Madjid A, Hakim L and Sabarudin A 2016 Preparation of chitosan beads using tripolyphosphate and ethylene glycol diglycidyl ether as crosslinker for Cr (VI) adsorption Chemistry and Chemical Technology 10 105-114
[7] Fajarwati F I, Kurniawan M A, Fatima M N and Fikrina R 2018 Penghilangan Zat Warna menggunakan Kompleks Polielektrolit Kitosan-Alginat JPSR: Journal of Pharmaceutical Science and Clinical Research 3 (1) 36-42
[8] 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 Indonesian Journal of Chemical Science 4 (1) 36-41
[9] Gheorghita Puscaselu R, Lobiuč A, Dimian M and Covasa M 2020 Alginate: From food industry to biomedical applications and management of metabolic disorders Polymers 12 (10) 2417
[10] Komariah A, Sriatun S and Pardoyo P 2017 Adsorpsi Alkil Benzena Sulfonat Menggunakan Zeolit Termodifikasi Cetyltrimethylammonium. Jurnal Kimia Sains dan Aplikasi, 20(1), 13-18.
[11] Kang Y G, Vu H C, Le T T and Chang Y S 2018 Activation of persulfate by a novel Fe (II)-immobilized chitosan/alginate composite for bisphenol A degradation Chemical Engineering Journal 353 736-745