Rhodamine-B Dyes Adsorption by Beads Alginate

Rahayu¹, Adriani Bandjar¹, Ninditha Clourisa Amaris Susanto², Feby Indah Fajarwati³, Nguyen Thi Thanh Phuong⁴

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Pattimura, Ambon, Indonesia
²Pharmacy Study Program, Vocational School, Universitas Sebelas Maret, Surakarta, Indonesia
³Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Islam Indonesia, Jogjakarta, Indonesia
⁴Institute of Environment and Resource, Vietnam National University of Ho Chi Minh City, Vietnam

*Corresponding author: rahayumahmud09@gmail.com

Received: 7 September 2021; Accepted: 8 April 2022; Published: 15 Juli 2022

Abstract

Research has been carried out on the adsorption of rhodamine-b dye by alginate beads. The production of alginate granules was carried out at a concentration of 3.5% alginate powder. Identification of functional groups was carried out by FT-IR and water absorption test resulted in a maximum capacity of 96.24% at 90 minutes. Determination of adsorption capacity was carried out by UV-VIS spectrophotometer at a maximum contact time of 30 minutes and a maximum pH at pH 7, and resulted in adsorption maximum concentration at 30 ppm is 15.954 mg/L with adsorption capacity of 4.7862 mg/g.

Keywords: Beads; alginate; adsorption; dye; rhodamine-b

Introduction

The natural wealth of the Indonesian territory, where the ocean is larger than the mainland, is capable of producing many types of seaweed. One of them is brown seaweed Padina sp. This type of seaweed contains an adequate amount of alginate, which potentially becomes a source of natural materials for alginate isolation. Alginate is a salt of alginic acid, which is composed of two monomeric units, namely β-D-mannuronic acid dan α-L-guluronic acid (Viswanathan & Nallamuthu, 2014). Alginate is a type of polysaccharide found in the cell walls of brown seaweed and plays an important role in maintaining the structure of cell tissue (Kurniasih et al., 2014).

Alginate is a natural polysaccharide possessing the characteristics to form hydrogels, costs inexpensive, tends to be biodegradable, and non-toxic (Popa et al., 2011). By having the hydrogel features, this material has the potential to form beads because the resulting shape is more well-structured (Yang et al., 2013). Beads have a large surface area which can increase the sensitivity to an interaction. If sensitivity to an interaction is a major concern, it is preferable to use beads. Beads are an easy and inexpensive modification of the supporting material form in the form of a polymer. Some applications demand sensitivity using beads; one of which is beads for mercury detection (Huang et al., 2014).
Beads can be used as adsorbents to overcome environmental problems such as industrial waste. Waste is expended material or residual substance from the process of making a product in industry or domestic waste that has less use-value. Most waste is removed in such a way that can pollute the environment (Kimia et al., 2013)(Nugroho, 2013). It is usually directly discharged into the waters so that it becomes a pollutant within the waters. This water pollution is a source of problems in life that accumulates from day to day and has a quite large impact on the stability of nature (Ramasubramaniam et al., 2012).

One of the wastes that often become environmental pollutants is the dye rhodamine-b. Rhodamine-b is a synthetic dye that is often used in the Batik industry. Rhodamine-b is a crystalline powder, odorless, greenish in its origin, purplish-red at high concentrations, and bright red at low concentrations (Kurniasih et al., 2014). Therefore, removing dye from waste is important. Adsorption methods have been widely chosen to overcome pollution problems because the process is safe, can be recycled, and does not require expensive and complicated equipment (Prambaningrum et al., 2009; Fajarwati et al., 2018; Adawiah et al., 2021).

**Making Alginate Beads**

Beads were made with 3.5 grams of alginate powder dissolved in 100 mL of aqua beads at a temperature of ± 80°C with stirring using a magnetic stirrer for 2 hours to produce a 3.5% alginate solution. Following it, the solution was put into a syringe while preparing a solution for printing beads that is a mixture of 1.5% (w/v) KCl solution and 100 mL CaCl2 2% (w/v) with a volume ratio of 2:1. The mixed solution of 1.5% (w/v) KCl and 2% (w/v) CaCl2 was first stored at 4°C. The distance between the tip of the needle and the surface of the printing solution was set at 3 cm. Beads were hardened within 15 minutes. After that, the beads were separated from the printing solution and stored in a closed container at room temperature (R.Darmawan et al., 2010; Clourisa et al., 2020).

**Water-Absorption Ability Test**

Beads were put into 10 mL of distilled water, continuously soaked for 30, 60, 90, 120, 150, 180, 210, and 1440 minutes. Beads were removed and weighed by wet weight at each immersion time.

**Studies on Adsorption**

**Producing Mother Liquor**

A total of 1 g of rhodamine-b was dissolved with 1000 mL of aqua beads in a 1000 mL volumetric flask to the mark so that a 1000 mgL⁻¹ methylene blue solution was obtained.

**Wavelength Measurement**

Measurement of the maximum wavelength of rhodamine-b was carried out by measuring the absorbance of rhodamine-b 3 mg L⁻¹ using a UV-Vis spectrophotometer. The wavelength with the maximum absorbance obtained would be used as the maximum wavelength for the next analysis.
**Manufacturing Standard Curve**

Rhodamine-b solution was made with a concentration of 1, 2, 3, 4, 5 mg L⁻¹. Then, the absorbance of each solution was measured using a UV-Vis spectrophotometer at the obtained maximum wavelength. Following this, a curve of the relationship between absorbance and concentration of rhodamine-b was made. The formed curve was used as a standard curve.

**Determination of Optimum Contact Time**

Alginate beads weighing 0.1 g were put into 25 mL of rhodamine-b solution with 10 mg L⁻¹. Then, it was shaken with a time variation of 5, 10, 15, 20, 30, 40, 45, 50, and 60 minutes. After the previous process of shaking, the beads were separated from the solution. The concentration of methylene blue remaining in the solution was measured using a UV–Vis spectrophotometer. The obtained optimum time would be used for further analysis.

**Determination of Optimum pH**

0.1 gram of Alginate beads were put into 25 mL of 10 mg L⁻¹ methylene blue with variations in pH of 3, 4, 5, 6, 7, and 8. The beads were then shaken until the optimum time had been previously obtained. After being shaken, the beads were separated from the solution. The concentration of rhodamine-b remaining in the solution was measured using a UV–Vis spectrophotometer.

**Determination of Adsorption Capacity of Na-alginate-chitosan PEC Film against rhodamine-b**

Alginate beads weighing 0.1 gram were put into 25 mL of rhodamine-b with various concentrations of 10, 20, 30, 40, and 50 mg L⁻¹ at the optimum pH, then shaken at the optimum contact time. After being shaken, the alginate beads were separated from the solution. The remaining concentration of methylene blue was measured using a UV–Vis spectrophotometer.

**Results and Discussion**

**Making Alginate Beads**

3.5% alginate beads were made by dissolving 3.5 grams of alginate powder with 100 mL of distilled water. The resulting solution was then put into a 10 mL syringe with a needle size of 0.5 mm. Bead printing was done with the distance of needle tip about ± 3 cm from the surface of the printer solution.

The printer solution was a mixture of solutions consisting of 1.5% KCl solution and 2% CaCl₂ solution with a volume ratio of 1:2. The solution processor had been made at a temperature of 40°C. Beads could be formed in about 5-10 minutes.

![Figure 1. (a). Beads in printer solution, (b). Dried Beads](image)

**Water Absorption Test**

This test was conducted to determine the hydrophilicity of alginate beads. This test was carried out by immersing the beads into distilled water at various times of 30, 60, 90, 120, 150, 180, 210, and 1440 minutes. The results of the water absorption test are presented in Figure 2.

![Figure 2. Data on water absorption by alginate beads](image)
The graph above shows that the water absorption capacity increases from the first 30 minutes to the next additional time and has a maximum water absorption capacity of 96.24% at the 90th minute. Furthermore, at the added time of more than 90 minutes, the absorption capacity decreases but the value is not significant and remains constant until 1440 minutes. This shows that the absorption capacity of alginate beads can occur well in aqueous media.

Characterization of Alginate Beads by FT-IR

![Figure 3. Spectra of FT-IR Beads alginate before and after adsorption](image)

The results of FT-IR characterization on commercial alginate before the adsorption showed absorption in the wavenumber area of 3264.73 cm\(^{-1}\) and 3300.77 cm\(^{-1}\) on beads after adsorption. This absorption area belongs to the characteristic of the O-H group. Furthermore, there is absorption at wavenumbers 1593.79 and 1614.25 cm\(^{-1}\) which indicates the absorption in the C=O functional group. This group also belongs to the characteristic functional group of the alginate structure. Absorption at wavenumbers 1407.45 and 1417.10 cm\(^{-1}\) indicates the absorption of the C-O group in C-O-H while the absorption in the wavenumber region is 1025.88-945.84 and 1087.13-943.46 cm\(^{-1}\) indicates absorption from the C-H group in C-C-H. Based on those wavenumbers, it can be seen that there has been a shift of absorption from each characteristic functional group of the alginate structure. This shows that there has been an adsorption process by alginate beads.

**Studies on Adsorption**

**Determination of wavelength**

Determination of wavelength was based on the range of the red-violet color area on the absorption wavelength of spectrophotometer UV-vis. The wavelength for rhodamine-b color was in the range of 500-560 nm. In this study, the absorbance measurement of rhodamine-b dye was carried out at a wavelength of 530 to 555 nm. The result of the maximum absorbance measurement of rhodamine-b dye was obtained at a wavelength of 545 nm with the highest absorbance value of 1,918. The results of the absorbance measurement in this range can be shown in Figure 3.

![Figure 4. Absorbance Graph of Maximum Wavelength](image)
Rhodamine-B Dyes Adsorption

Manufacturing Standard Curve

The standard curve measured in this study was conducted at the obtained maximum wavelength; that is 545 nm with a concentration of 1, 2, 3, 4, 5 mg L\(^{-1}\). The results of the standard curve measurements are presented in Figure 4. The measurement results showed that the obtained regression equation was \(y = 0.1376x + 0.0164\) with R\(^2\) percentage by 99.61%.

![Figure 5. Rhodamine-B Standard Curve](image)

**Determination of Optimum Contact Time**

The impact of contact time was analyzed by interacting 0.1 gram of alginate beads into 25 mL of the rhodamine-b solution of 10 mg L\(^{-1}\) and shaken at 200 rpm for 5, 10, 15, 20, 30, 40, and 50 minutes. The adsorption capacity of alginate beads at this variation of contact time is presented in Figure 6.

![Figure 6. Adsorption of rhodamin-b by alginate beads on contact time variation](image)

Based on the data in Figure 6, the adsorption capacity of rhodamine-b by alginate beads increased with the rise of interaction contact time. It can be seen in Figure 6 that in the first 5 minutes there has been adsorption of rhodamine-b and as the contact time rises, the adsorption process increases too. This occurred because the active site contained in the beads was still available, so the ability of the beads to interact with rhodamine-b continued to increase. This adsorption process continued until the optimum contact time of the interaction of beads with rhodamine-b was obtained. After reaching the optimum contact time, the active sites on the beads began to fill up so that in the additional time after the optimum contact time, the active sites on the beads began to saturate and the adsorption began to decrease.

The optimum contact time obtained was 30 minutes with the adsorption capacity of rhodamine-b of 1,283 mg/L. In the adsorption process, the decrease in adsorption capacity could be due to the possibility that not all the presence of adsorbate could be bound to the adsorbent so what happened in this process was an electrostatic bond which could allow physical adsorption to occur. Therefore, it is also possible to re-release the adsorbate for a long time on the saturated adsorbent (Safitri, 2019).

**Determination of Optimum PH**

Determination of the optimum pH was studied by shaking the beads of 0.1 g in 25 mL of 10 mg/L rhodamine-b solutions. Shaking was carried out at a speed of 200 rpm for an optimum contact time of 30 minutes or a previously obtained time. The pH used in determining the optimum pH is in the range of acidic to basic pH, which was at 4 to pH 9. The results of adsorption at various pH variations are shown in Figure 7.
Based on the data in Figure 7, the adsorption capacity of rhodamine-b by alginate beads increased as the pH of the interaction solution increased. It can be seen in Figure 7 that at pH 4 there has been adsorption of rhodamine-b and as the pH increases, the adsorption process rises. Changes in the pH of the solution did not only affect the charge of the adsorbate but also affect the charge of the adsorbent. Rhodamine-b is a cationic dye, so the adsorption capacity at pH < 4 is low. This is due to the competition between H⁺ and rhodamine-b to occupy the active site of the alginate beads. The low adsorption of rhodamine-b at pH > 9 was due to the competition between OH⁻ ions and adsorbent to bind with rhodamine-b. The number of OH⁻ ions contained in pH > 9 solutions was increasing. This caused the interaction between the alginate beads and OH⁻ to expand so that the interaction between rhodamine-b and the active site of the alginate beads was disrupted.

At pH 7, the adsorption ability of alginate beads on rhodamine-b reached the optimum state. The reason was that in this state, the solution was in a neutral pH condition where there was no competition for H⁺ ions and OH⁻ in the solution which interfered with the beads adsorption process for rhodamine-b. The adsorption capacity at pH 7 resulted in an adsorption value of 4.5959 mg/L.

**Determination of Optimum Concentration**

Determination of the optimum concentration was studied by shaking at 0.1 g of alginate beads at the optimum pH, namely pH 7 and shaken during the optimum contact time, which was for 30 minutes. The concentration variation used is from 10 – 50 mg/L with an interval of 10 mg/L. The results of adsorption at various concentrations are presented in Figure 8.

Figure 8 shows that when the concentration of rhodamine-b increases, the adsorption capacity increases, but at concentrations over 30 mg/L, the adsorption capacity begins to decrease. It was because the quantity of rhodamine-b molecules grows while the number of active sites in the alginate beads remains constant. The number of contacts with the accessible active site will grow as the concentration of adsorbate increases. The growth will continue until the adsorbent site becomes saturated. At a concentration of 30 mg/L, the adsorption capacity is 15.9540 mg/L, or 4.7862 mg/g. Tanasale (2014) found that the optimum adsorption capacity of rhodamine-b by activated carbon from durian skin was 48.67 mg/L in a study on the adsorption of rhodamine-b by activated carbon from durian skin.
Conclusions

The highest proportion of alginate beads to absorb water occurred at the nineteenth minute, at 96.24 percent adsorption efficiency. The optimum contact time in the adsorption process of rhodamine-b dye by alginate beads would be 30 minutes at an adsorption concentration of 1.28 mg/L, with the optimum pH at pH 7 at an adsorption concentration of 4.5959 mg/L. Even the maximum adsorption capacity occurs at a concentration of 30 ppm at an adsorption capacity of 4.7862 mg/g.

References

Adawiah, S. R., Sutarno, S., Nur, A., Gani, R., & Andriani, T. (2021) 'Comparative Study of Adsorption-Desorption of Nitrate and Sulfate Anions on Modified Bentonite', Walisongo Journal of Chemistry, 4(1), pp. 23-31. https://doi.org/10.21580/wjc.v4i1.758

Clourisa, N., Susanto, A., Siswanta, D., (2020). 'Manufacture and Optimization of Water Dissolved Ferrous Metal Color Sensors with Cargueenan Matrix', Jurnal Ilmiah Teknik Kimia, 4(2).

Fajarwati, F. I., Kurniawan, M. A., Fatima, M. N., & Fikrina, R. (2018) 'Removal of Dyes using Chitosan-Alginate Polyelectrolyte Complex', JPSCR: Journal of Pharmaceutical Science and Clinical Research, 3(1), 36. https://doi.org/10.20961/jpscr.v3i1.16

Huang, X., Hao, Y., Wu, H., Guo, Q., Guo, L., Wang, J., Zhong, L., Lin, T., Fu, F., & Chen, G. (2014). 'Magnetic Beads-Based Colorimetric Detection of Mercuric Ion', Sensors and Actuators, B: Chemical, 191, 600–604. https://doi.org/10.1016/j.snb.2013.10.025

Nugroho, D., (2013) 'Biosand Filter Reactor To Reduce Levels of Metal Ion Fe³⁺ And Zn²⁺ in Industry', Skripsi, UNNES, Semarang.

Kurniasih, M., Riapanitra, A., & Rohadi, A. (2014). 'Rhodamine B Adsorption with Chitosan Powder and Beads Chitosan Adsorbent', Sains Dan Matematika, 2(2), 27–33.

Popa, E. G., Gomes, M. E., & Reis, R. L. (2011) 'Cell Delivery Systems Using Alginate-Carrageenan Hydrogel Beads And Fibers For Regenerative Medicine Applications', Biomacromolecules, 12(11), 3952–3961. https://doi.org/10.1021/bm200965x

Prambaningrum, W., Khabibi, K., & Djunaidi, M. C. (2009) 'Adsorption of Ion(III) and Cadmium(II) Ions Using Chitosan Gel', Jurnal Kimia Sains Dan Aplikasi, 12(2), 47–51. https://doi.org/10.14710/jksa.12.2.47-51

R.Darmawan, Widjaja, T., Mulyanto, & Ardiansyah, E. T. (2010) 'Comparative Study of Continuous Ethanol Production Using Mutated Z.Mobilis Cell Immobilization Technique: Ca-Alginate And K-Carrageenan', Rekayasa Kimia Dan Proses, 1–6.

Ramasubramaniam, S., Govindarajan, C., Gomathi, T., & Sudha, P. N. (2012). Removal of Chromium (VI) from Aqueous Solution using Chitosan - Starch Blend', Der Pharmacia Lettre, 4(1), pp. 240–248.

Tanasale, M., Sutapa, I. W., Tuptawry, R.R. (2014) 'Adsorption of Rhodamine B dye by Activated Carbon from Durian Peel (Durio zybetinus)', Ind. J. Chem. Res., 2014, 2, 116 - 121. 116–121.
Safitri, S. R. (2019) ‘The Effect of Time Variations on the Ability of Banana Heart (Musa Spp) as an Adsorbent for Dyes Waste’, 3(2).

Viswanathan, S., & Nallamuthu, T. (2014). Extraction of Sodium Alginate from Selected Seaweeds and Their Physiochemical and Biochemical Properties. 3(4), 10998–11003.

Yang, B., Lu, Y., Ren, T., & Luo, G. (2013). One-Step Synthesis of PH-Sensitive Poly(Acrylamide-co-Sodium Acrylate) Beads with Core-Shell Structure. *Reactive and Functional Polymers, 73*(1), 122–131. https://doi.org/10.1016/j.reactfunctpolym.2012.08.012