

The Utilization of Duck Egg Shell Waste as A Methylene Blue Bioadsorbent

Ibnu Fharizi*, Farikha Maharani, Safa'ah NurFa'izin, Indah Hartati

Chemical Engineering Department, Engineering Faculty, Universitas Wahid Hasyim
Jl. Raya Gunungpati No.KM.15, Nongkosawit, Semarang, Central Java, Indonesia 50224

*Email : IbnuAarizi05@gmail.com

Abstract

The development of the textile industry in Indonesia has experienced a significant increase since the 1980s. From the non-oil and gas sector, the textile industry is the largest source of government revenue. In addition to its growth and impressive increase, there are around 10-15% of used textile dyes are thrown away and become waste during the dyeing or coloring process which can exceed the maximum Chemical Oxygen Demand level of 150 mg/L. Synthetic dyes contain carcinogenic substances that can damage the environment and aquatic biota. An alternative for handling dye waste is the adsorption method using bioadsorbent from duck eggshells. The content contained therein has the potential to be used as a bioadsorbent because it has active groups, abundant amounts, and is economical. This study aims to determine the effect of process variables such as adsorbent mass ratio, contact time, and pH on the adsorption capacity of methylene blue using duck eggshells using the UV-Vis Spectrophotometer analysis method. The results of the study showed that the optimal conditions for the adsorption of 30 ppm methylene blue were an adsorbent mass ratio of 8 grams, a contact time of 60 minutes, and a pH of 3. The adsorption capacity obtained was 90.8591%, which reduced the concentration of methylene blue to 0.187 ppm.

Keywords: *adsorption, methylene blue, duck eggshell, bioadsorbent*

INTRODUCTION

This research relates to environmental issues and waste management. Methylene Blue is a synthetic dye widely used in the textile, pharmaceutical, and other industries. This dye is often found in industrial waste and can pollute the environment if not properly treated before being discharged. Much research has been conducted to find effective and efficient methods for removing this dye from waste. One method that has been widely developed is the use of bioadsorbents, which are natural materials that can absorb dyes from waste.

Various methods are used to treat waste containing synthetic dyes, including biological, physical, and chemical methods such as adsorption, biosorption, coagulation/flocculation, advanced oxidation, ozonation, membrane filtration, and liquid-liquid extraction. The advantages and disadvantages of each method have been widely discussed (Salleh et al., 2011). Adsorption is a physical method widely used to treat waste containing dyes due to its ease of use, efficiency, low energy

requirements, and the ability to utilize various adsorbent materials (Teng and Low, 2012; Liu et al., 2012).

Duck eggshells are a natural material with potential as a biosorbent for removing Methylene Blue dye from wastewater. Duck eggshells contain high levels of calcium carbonate, which can bind to Methylene Blue dye through adsorption.

Currently, extensive research has been conducted to obtain adsorbent materials that are relatively easier to obtain than activated carbon. Adsorbents can be made from organic materials such as grass, leaves, flowers, and fruit peels, which are readily available in abundance. Solid organic materials that have been studied as adsorbents include coconut fronds (Hameed et al., 2008), hazelnut husks (Dogan et al., 2009), rice bran (Chowdhury et al., 2011), and cogongrass (Li et al., 2013). Cogongrass, or cogongrass (*Imperata cylindrical*), is a weed found in agricultural fields.

This study aims to test the effectiveness of duck eggshells as a biosorbent for removing Methylene Blue dye from solutions. Using natural materials such as duck eggshells as a biosorbent is expected to help reduce environmental pollution from industrial waste containing Methylene Blue dye. Furthermore, this research can provide an environmentally friendly and low-cost alternative for waste treatment.

RESEARCH METHODS

Materials

This study used materials such as distilled water, eggshells, rice husks, methylene blue (Merck), HCl (Merck, 37%), and NaOH (Merck, 99%). The equipment used included glassware, an oven, a hotplate, a magnetic stirrer, a mortar, a porcelain cup, an analytical balance, a 100-mesh sieve, and a UV-Vis spectrophotometer.

Research Procedure

1) Adsorbent preparation

- Clean the duck eggshells using clean, running water to remove any membranes and dirt adhering to them.
- Dry the duck eggshells in the sun.
- Crush the dried duck eggshells.
- Sift them using a 100-mesh sieve.

2) Adsorbent activation

After preparation, the eggshells were separately activated with 0.1 M HCl for 24 hours. They were then filtered through filter paper and rinsed with distilled water until the pH was neutral. The adsorbent pores were then activated by oven-drying at 105°C for 2 hours.

3) Adsorbate preparation

• Stock solution of *Methylene Blue*

Methylene blue with a concentration of 1000 ppm is made by dissolving 100 g of methylene blue in 100 mL of distilled water. The solution is then transferred to a 100 mL volumetric flask.

• Standard solution of *Methylene Blue*

Make a 100 ppm methylene blue solution by taking 10 mL of methylene blue stock solution and diluting it into a 50 mL volumetric flask. The 100 ppm methylene blue solution is diluted again into smaller concentrations of 10, 20, 30, 40, 50, and 60 ppm in a 50 mL volumetric flask.

4) termination of optimum wavelength of *Methylene Bule*

A 50 mL methylene blue solution, starting with the smallest concentration of 10 ppm, was measured at 600-700 nm using a UV-Vis spectrophotometer. The highest absorbance was determined as the optimum wavelength.

5) Proses Adsorpsi

The adsorption of methylene blue was carried out at various adsorbent mass ratios, contact time, pH, and adsorbate concentration using a stirring process on a hotplate at room temperature. Measure the absorbance of the methylene blue solution using a UV-Vis Spectrophotometer at the optimum wavelength before and during the adsorption process. After a predetermined time, the solution was then filtered using filter paper. Measure the absorbance of the filtrate. The determination of the optimum conditions was selected from the largest decrease in absorbance.

- **The determination of optimum mass of adsorbent**

Prepare adsorbent samples with duck eggshell mass ratios of 4, 6, 8, and 10 grams. Then, add 50 mL of 30 ppm methylene blue dye solution into a 250 mL Erlenmeyer flask. The pH of the solution corresponds to the pH of the distilled water solvent, which is pH 7. The adsorption process is carried out for 30 minutes.

- **Optimum contact duration determination**

The results of the optimum adsorbent mass ratio were used to determine the optimum adsorption capacity with time variations of 30, 45, 60, and 75 minutes at the same pH as the pH of distilled water, namely pH 7.

- **Optimum pH determination**

The results of the adsorbent mass ratio and optimum contact time were used to determine the optimum pH with pH variations of 3; 5; 7; 10.

6) UV-Vis analysis

The UV-Vis analysis test aims to compare the initial color of the methylene blue substance with that after undergoing an adsorbance process by adding mass, contact time, and pH of the activated duck eggshell powder.

7) Data analysis

To determine the effectiveness of duck eggshells as an adsorbent, absorbance measurements are required on the methylene blue solution after the adsorption process using a UV-Vis Spectrophotometer. The measurement results are used to calculate the adsorption capacity and power. The adsorption capacity can be obtained through equation (1):

$$q = \frac{V(C_0 - C_e)}{m} \dots \dots \dots (1)$$

with:

qe = adsorption capacity (mg/g)

V = volume of methylene blue solution
m = mass of adsorbent (g)

C0 = concentration of methylene blue solution before adsorption (mg/L)
Ce = concentration of methylene blue solution after adsorption (mg/L)
Meanwhile, the adsorption power is obtained using equation (2):

$$D = \frac{C_0 - C_e}{C_0} \times 100\% \dots \dots \dots (2)$$

with:

D = Adsorption power percentage (%)

RESULT AND DISCUSSION

Effect of Mass of the Adsorbent

In general, the greater the mass of adsorbent used, the greater the adsorption capacity and efficiency. However, in this study, the effect of adsorbent mass on the percentage (%) of methylene blue removal in Figure 1 shows that at a mass of 4 g to 8 g, the adsorption efficiency increased and decreased. The initial addition of 4 g gave a maximum value with a methylene blue adsorption percentage of 86.63%. According to (R. Bhaumik, 2019), this can occur because increasing the amount of adsorbent increases the active sites on the adsorbent surface, so that the greater the amount of adsorbent, the more methylene blue will be adsorbed. However, under certain conditions, the absorption percentage will remain constant or even decrease, due to saturation of the adsorbent. This is seen in the mass of 4 g to 10 g, which experienced an increase and a decrease in the absorption of methylene blue levels absorbed in activated duck eggshell powder. At a mass of 8 grams is the best mass with a percentage result reaching 89.8% adsorbance, because during the adsorbance process there is an equilibrium between the methylene blue absorbed by the duck eggshell powder adsorbent and the amount of methylene blue remaining in the solution, so that the duck eggshell powder adsorbent has optimally bound the methylene blue.

After the adsorption process reaches optimal results, the percentage reduction in methylene blue content decreases, specifically at a mass of 10 grams. This decrease can occur because the concentration of methylene blue in the solution is insufficient to fill all active sites of the adsorbent and the presence of clumping, which causes a decrease in the effective surface area for methylene blue absorption (Siringo-ringgo, 2019).

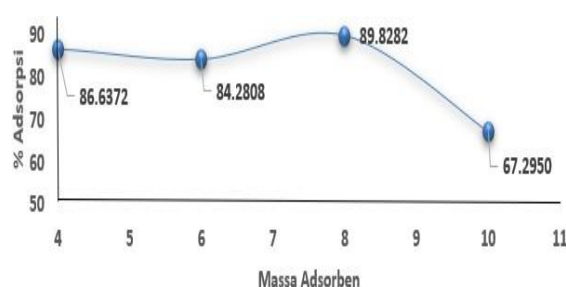


Figure 1. Percentage of the adsorption at different adsorbent mass

However, if the mass of the biosorbent is continued to be increased after reaching a certain mass, its adsorption capacity will decrease. This occurs because the biosorbent is saturated with adsorbent in the methylene blue solution, and adsorbent particle aggregation occurs, causing a decrease in the total surface area. Furthermore, particle aggregation also causes the desorption of weakly bound adsorbates on the adsorbent surface.

From several literatures and studies that have been conducted, there are many factors that can influence this, the decreased adsorption capacity can be caused because at a certain mass there are still many active substances that have not bound to the adsorbate and adsorbate clumping occurs, so that the adsorption efficiency is getting smaller, while at a mass with the right dosage according to the level to be absorbed will increase the effectiveness of the adsorption process and there will be an even distribution of the adsorbent surface that will be bound to the adsorbate maximally. In addition, the overall adsorption capacity produced tends to decrease as the biosorbent mass increases (Mariadas et al., 2019).

Effect of time of contact

One factor influencing the adsorption process is contact time. The more collisions that occur, the faster the reaction proceeds until equilibrium is reached. Equilibrium between adsorption and desorption rates occurs as time reaches its optimal results. The ability of activated duck eggshell powder as an adsorbent, influenced by contact time, can be seen in Figure 2.

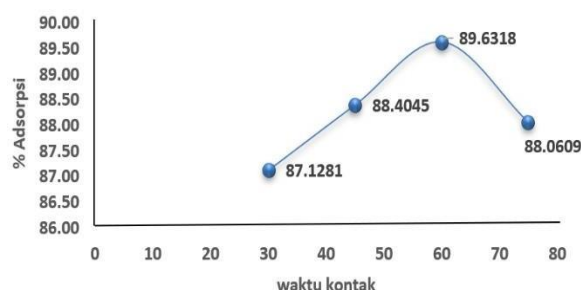


Figure 2. Percentage of the adsorption at different contact duration

Figure 2 shows that the concentration of adsorbed methylene blue increases with time. This occurs because the longer the collision between the activated duck eggshell powder and the methylene blue, the more methylene blue is adsorbed by the activated duck eggshell powder. The best result was 89.631% for adsorbing methylene blue dye at a concentration of 30 ppm, with a contact time of 60 minutes. These results are supported by the results of Falahiyah's (2019) study on methylene blue adsorption with coconut fiber and shell ash, which yielded an optimum time of 60 minutes.

At contact time variations of 30, 45, and 60 minutes, there was an increase, then at 75 minutes it decreased. This occurs because after passing the optimal contact time, the adsorbate will undergo a process of release from the adsorbent surface called desorption. The cause of desorption is because the adsorbent on its surface has become saturated, so that the adsorbent molecules will return to the solution (Siringo-ringgo, 2019). Desorption is the process of releasing ions or molecules attached to the adsorbent. This process is usually carried out to regenerate the adsorbent so that it can be reused after saturation.

Effect of pH

Figure 3 shows that the concentration of adsorbed methylene blue dye increases and decreases with increasing acidity. The highest adsorption capacity was obtained at pH 3 where the adsorbed methylene blue was 90.859%. The cationic properties of methylene blue are only visible at acidic pH. Cationic itself is a type of surfactant that when in aqueous solution will produce positively charged ions, especially quaternary nitrogen compounds such as amine compounds which tend to be basic.

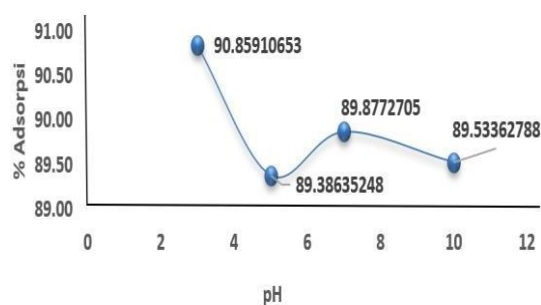


Figure 3. Percentage of the adsorption at different pH

Adsorption at high pH decreases because the adsorbent surface area is protonated more and there is competition for adsorption between H⁺ ions and free methylene blue ions and OH⁻ ions for their binding sites. Therefore, H⁺ ions react with functional anionic groups on the adsorbent surface, reducing the number of methylene blue ions that can be bound (Jirekar et al., 2019).

At low pH (less than 5), methylene blue ions can enter the adsorbent pore structure, while at high pH (10 or more than 7), the zwitter ion form of methylene blue increases aggregation to form larger molecules (dimers), making it more difficult to enter the adsorbent pores. This occurs because ionized methylene blue in water becomes positively charged (C₁₆H₁₈N₃S⁺), allowing it to bind to the negatively charged adsorbent surface, thereby increasing adsorption capacity and power (Riapanitra et al., 2019). Meanwhile, at high pH, the surface of the eggshell adsorbent will be negatively charged so that they repel each other due to the methylene blue ionizing into negative ions (Cl⁻) (Nurlaili et al., 2020).

The results of this experiment were supported by Hadayani et al. (2018) who conducted methylene blue adsorption using coffee pulp xanthate compounds as adsorbents, stating that the adsorption rate would increase with decreasing acidity levels.

CONCLUSION

The adsorption method is an alternative method that can be used to reduce the content of dissolved dyes in liquid textile wastewater, where in this study using a solution of methylene blue in solution as an experimental material. In the adsorption of liquid methylene blue dye with adsorbents from duck eggshells, it was proven to be able to reduce the concentration of the solution from 30 ppm in 50 mL to 3.03682 ppm so that it can replace activated carbon adsorbents that are difficult to degrade. The optimum operating conditions for the adsorption of 30 ppm methylene blue are an adsorbent mass ratio of 8 grams, a contact time of 60 minutes, and a pH of 3. The adsorption capacity obtained was 90.8591%, which reduced the concentration of methylene blue to 0.187 ppm. The potential of the material as a bioadsorbent is supported by the presence of pores and active groups.

REFERENCE

- Angraini, S. (2022). Pemanfaatan Limbah Cangkang Telur dengan Ampas Tebu sebagai Adsorben Zat Warna Methylene Blue dalam Limbah Tekstil.
- Amalia, V. N. (2021). *Pemanfaatan Limbah Cangkang Telur Ayam sebagai Adsorben untuk Menurunkan Kadar Besi (Fe) dengan Sistem Batch* (Doctoral dissertation, UIN Sunan Ampel Surabaya).
- Amanah, I. N., Indriyani, F. I. P., & Asriza, R. O. (2022, December). Pengaruh Jenis Asam pada Aktivasi Cangkang Telur sebagai Adsorben Logam Cu pada Air Kolong. In *PROCEEDINGS OF NATIONAL COLLOQUIUM RESEARCH AND COMMUNITY SERVICE* (Vol. 6, pp. 117-122).
- Aritonang, B., Sijabat, S., & Ritonga, A. H. (2019). Efektivitas arang aktif cangkang telur bebek dan kulit durian sebagai adsorben untuk menurunkan kadar bilangan peroksida dan asam lemak bebas pada minyak goreng bekas. *JURNAL KIMIA SAINTEK DAN PENDIDIKAN*, 3(1), 28-32.
- Ariyanto, A. A. (2020). *PENGUNAAN CANGKANG TELUR DAN ZEOLIT SEBAGAI ADSORPEN LOGAM MANGAN DAN KADMIUM PADA AIR LIMBAH LABORATORIUM* (Doctoral dissertation, Universitas PGRI Adibuana Surabaya).

- Fadhil, D. H., Al-Hussin, A., & Yousif, E. (2019). Removal of methylene blue dye from water using ecofriendly waste product (Eggshell) as an adsorbent and using the optimum adsorption conditions with real water sample from Tigris river. *Al-Nahrain Journal of Science*, 22(1), 9-14.
- Fasihah, N. S. (2023). *PENGUNAAN CANGKANG TELUR AYAM SEBAGAI ADSORBEN PADA PENGOLAHAN LIMBAH INDUSTRI LAUNDRY* (Doctoral dissertation, Sultan Ageng Tirtayasa).
- Lestari, N. C., Budiawan, I., & Fuadi, A. M. (2021). Pemanfaatan cangkang telur dan sekam padi sebagai bioadsorben metilen biru pada limbah tekstil. *Jurnal Riset Kimia*, 12(1), 36-43.
- Marintika, G. F., & Melwita, E. (2021). PEMISAHAN PEWARNA NAFTOL DARI LIMBAH KAIN JUMPUTAN DENGAN BIOSORBEN CANGKANG TELUR. *Applicable Innovation of Engineering and Science Research (AVoER)*, 117-122.
- Nurlaili, T., Kurniasari, L., & Ratnani, R. D. (2017). Pemanfaatan limbah cangkang telur ayam sebagai adsorben zat warna methyl orange dalam larutan. *Jurnal Inovasi Teknik Kimia*, 2(2).
- Parlindungan, J. Y., Pongkendek, J. J., Wairara, S., & Abdullah, N. (2019, October). Encapsulation powder skin duck eggshells on alginate as adsorbent methylene blue. In *IOP Conference Series: Earth and Environmental Science* (Vol. 343, No. 1, p. 012194). IOP Publishing.
- Parvin, S., Rubbi, M. F., Ruman, M. A., Rahman, M. M., & Biswas, B. K. (2020). Utilization of egg-shell, a locally available biowaste material, for adsorptive removal of congo red from aqueous solution. *Aceh International Journal of Science and Technology*, 9(2), 63-74.
- Praipipat, P., Ngamsurach, P., Saekrathok, C., & Phomtai, S. (2022). Chicken and duck eggshell beads modified with iron (III) oxide-hydroxide and zinc oxide for reactive blue 4 dye removal. *Arabian Journal of Chemistry*, 15(11), 104291.
- Putra, A. S. P., Munir, R., & Natalisanto, A. I. (2022). Studi Adsorpsi Logam Berat Besi (Fe) dan Timbal (Pb) Air Sungai Mahakam oleh Limbah Cangkang Telur dan Abu Gosok. *Progressive Physics Journal*, 3(2), 179-183.
- Purwaningsih, D. Y., Wulandari, I. A., & Aditya, A. W. (2021, March). Pemanfaatan Cangkang Telur Ayam Sebagai Biosorben untuk Penurunan COD pada Limbah Cair Pabrik Batik. In *Prosiding SENASTITAN: Seminar Nasional Teknologi Industri Berkelanjutan* (Vol. 1, No. 1, pp. 507-512).
- Rahman, N. A., Pardede, E. P., & Mularen, A. (2022). Pemurnian Minyak Jelantah Menggunakan Adsorben Berbasis Cangkang Telur. *Prosiding SENIATI*, 6(4), 785-793.
- Ramdani, W. W., Wardani, G. A., & Fathurohman, M. (2022, December). Arang Aktif Cangkang Telur Bebek Termodifikasi Tween 80 sebagai Adsorben Tetrasiklin Hidroklorida. In *Prosiding Seminar Nasional Diseminasi Hasil Penelitian Program Studi S1 Farmasi* (Vol. 2, No. 1).
- Riwayati, I., Fikriyyah, N. M., & Suwardiyono, S. (2019). Adsorpsi Zat Warna Methylene Blue Menggunakan Abu Alang-Alang (*Imperata cylindrica*) Teraktivasi Asam Sulfat. *Jurnal Inovasi Teknik Kimia*, 4(2).
- Vadeesirisak, C., Chayabutra, S., & Sirirak, J. (2021). Utilization of Duck Eggshell Powder as Natural Adsorbent for the Removal of Acid and Basic Dye from Water. *Burapha Science Journal*, 26(2), 837-851.