Journal of Tropical Pharmacy and Chemistry

Journal homepage: https://jtpc.farmasi.unmul.ac.id

Adsorptive Removal of Chemical Oxygen Demand Using Eggshells and Tea Waste Entrapped in Calcium Alginate

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Abstract

This study aims to assess the efficiency of two agricultural wastes as biosorbents to remove the chemical oxygen demand (COD) from a batik wastewater sample. COD-containing batik wastewater was treated with a combination of biosorbents by eggshells and tea waste activated using H_2SO_4 and then immobilized in calcium alginate through the entrapment technique. The contact time, pH, and biosorbent dose were all investigated to examine the efficiency of biosorbent to remove COD. The independent variables for the optimization process are the contact time (47.13, 50, 60, 70, and 72.87 min), pH of the samples (1.71, 2,3, 4, and 4.28), and the ratio of the number of biosorbent between eggshells: tea waste (2.67:12.33, 3.75:11.25, 7.5:7.5, 11.25:3.75, and 12.33:2.67). The Characterization of the biosorbents was investigated using scanning electron microscopy (SEM), Fourier transforms infrared spectroscopy (FTIR), and energy-dispersive x-ray (EDX) analysis. The results show that eggshells and tea waste immobilized by calcium alginate with a ratio of 2.67 g: 12.33 g, a contact time of 60 min, and a sample pH of 3 are 89% effective in removing the COD in batik wastewater samples.

Keywords: Agriculture waste, Biosorption, Calcium alginate, Wastewater

Received: 29 August 2022 **Accepted**: 10 May 2023

DOI: https://doi.org/10.25026/jtpc.v7i2.480

How to Cite:

Fatmawati, Z., Ariyanto, H. D., Paramita, V., 2023. Adsorptive Removal of Chemical Oxygen Demand Using Eggshells and Tea Waste Entrapped in Calcium Alginate. *J. Trop. Pharm. Chem.* **7**(2). 67-77. **DOI**: https://doi.org/10.25026/jtpc.v7i2.480

1 Introduction

Batik is declared one of Indonesia's cultural treasures. Batik was born from two words: "amba", which means to write, width, area and "tik" or "nitik", which has the meaning of dot or drip; therefore, it can be defined as writing or making dots with wax on a wide cloth [1]. On October 2, 2009, the United Nations (UNESCO) recognized batik internationally as *an Intangible Cultural Heritage* (ICH). The existence of official recognition from UNESCO caused the demand for batik to increase compared to previous years [2].

According to data from the Ministry of Industry, batik exports from January to June 2019 reached 17.99 million US dollars and from January to July 2021 came 21.54 million US dollars [2]. The increasing demand is a driver of batik business expansion in Indonesia [3]. The increased batik industry in Indonesia is directly proportional to the rise in production and a large amount of waste left over from production.

Waste left over from the production of the batik industry is usually a waste liquid from the processing phase of fabric dyeing with *nonbiodegradable* artificial dyes that have the potential to damage the environment. Most batik industry players do not process the remaining production waste due to the expensive cost left over-processing waste and difficulties in processing methods[4]. Waste left over from batik industry production contains harmful chemical compounds in the form of heavy metals that can increase the value of *Chemical Oxygen Demand* (COD) and *Biological Oxygen Demand* (BOD) H_2O to disrupt aquatic ecosystems and harm the surrounding community [2]. Based on Peraturan Menteri Lingkungan Hidup and Kehutanan Republik Indonesia Nomor P.16 / MENLHK / SETJEN / KUM.1 / 4/2019 concerning Quality Standards for waste remaining production for COD parameters of 150 mg / L [5].

In the case of excessive *levels of Chemical Oxygen Demand* (COD) and exceeding the quality standards of batik production waste, then in order for the remaining production waste to be disposed of into water bodies, it must first be processed and treated [4]. In general, waste from production in the form of liquids can be processed and processed by chemical, physical, as well as biological means. The application of each method depends on the characteristics of the waste left over from the liquid production itself [6].

One of the efforts to treat waste leftover production containing harmful chemical compounds from the batik staining process is adsorption processing. Adsorption technology has become one of the most attractive due to its excellent performance, low power consumption and easy operation [7]. One of the many adsorbents generally used is activated carbon, but it is currently favoured to study adsorption by utilizing biosorbents [8]. Bio sorbent is one of the adsorption methods by using natural substances or compounds such as clay, chitosan, zeolite, activated carbon, and other waste substances or mixtures left over from products that come from various industries such as egg shells, bagasse, and agricultural biomass such as seeds, fruit peels and so on [9].

Scientific studies on the use of eggshells and tea pulp as biosorbents have been widely carried out, such as the use of eggshells by purwaningsih [3] which investigates the mechanism of eggshell adsorption in reducing COD levels in waste leftovers from batik factory liquid production with egg shells as activated carbon activated with H_2SO_4. The results showed an optimal biosorbent mass of 5%, with COD levels falling by 87% with a contact time of 60 minutes.

In addition, tea pulp as a bio sorbent absorbing Fe and Pb metals [10] with tea pulp as it gave activated carbon an activation treatment of HCl 0.1 N, then analyzed the effectiveness of adsorption by considering the adsorbent mass and contact time. The results obtained tea pulp bio sorbents effectively lower Fe and Pb.

The adsorption method that it can do today is to modify activated carbon formed by utilizing acid activation and reprocessed by mobilization. Previous scientific studies used this method [11] where adsorbents from activated carbon were immobilized with ca-alginate and then analyzed COD levels and phosphate metals, which fell based on contact time, pH, concentration, adsorbent mass and stirring speed. The results obtained by adsorption data are more suitable for analysis with the Freundlich equation and are effective for removing metal phosphates and reducing COD levels.

Previous scientific studies served as the basis for current scientific studies. Then scientific studies were developed using eggshells, and tea dregs with the activation method of ca-alginate mobilized acid to reduce COD levels in industrial batik waste leftover liquid production. With the entrapment method by utilizing ca-alginate, it is hoped that bio sorbents have advantages, including having mechanical strength, can form strong aggregates, rigidity, size and porosity characteristics. This advantage can increase absorption capacity, facilitate the separation of bio sorbents from solutions, are immune to the chemical environment, and can be readily adsorbed [12]. he analysis that will be carried out includes an analysis of the characteristics of bio sorbents, namely water and ash content and commentary on cod levels of the waste left over from batik industry liquid production to determine the absorption ability of bio sorbents with variations in bio sorbent mass, contact time and pH. With this scientific study, it is hoped that it will be able to form highly effective bio sorbents, cheap and easy to use.

In chemistry, *Chemical Oxygen Demand* (COD) is the amount of O_2 required to perfectly *oxidize* compounds made from living organisms/creatures contained in one litre of water sample [13]. This is a measure of H_2O pollution caused by compounds made from living organisms/animals that can naturally *be oxidation* by the microbial processing phase, which results in O_2 dissolved in H_2O, which goes down [14]. COD levels in residual waste that pass quality standards indicate that the waste leftover liquid production has a high concentration of elements made of living organisms /creatures and those made of organisms / living things [15].

These chemical substances or compounds are very accumulative and difficult to decompose. If a person is often exposed to water with high COD levels, substances or chemical compounds that pollute accumulate in the human body, causing disturbances in human health [16]. Many scientific studies have been conducted to find substances or compounds that can lower COD and BOD levels in the water. One of the substances or compounds of concern is eggshells and tea pulp, which in previous scientific studies only utilized one of the substances or compounds. No scientific studies have discussed the merger of these two substances or compounds with the mobilization of Ca-alginate. The method widely practiced before was the activation of utilizing acids without immobilization; there is no surefire method to form an efficient biosorbent for COD absorption. This scientific study was later used to create biosorbents with an acid activation processing phase mobilized utilizing Ca-alginate.

2 Materials and Methods

2.1 Materials

The materials included eggshells and tea waste obtained from some restaurants in Semarang (Indonesia). The chemicals used in the production of biosorbent preparation, namely sulfuric acid (H_2SO_4) and calcium chloride ($CaCl_2$) were purchased from Merck & Co., Inc. (New Jersey, US), and sodium alginate was purchased from HiMedia Laboratories Pvt. Ltd. (Mumbai, India). Batik wastewater used in this study was obtained from one of the batik industries in Kampung Batik Laweyan (Surakarta, Indonesia).

2.2 Experiments

The production of the biosorbent includes three steps: 1) eggshell and tea waste preparation into powder, 2) activation with H_2SO_4, and 3) immobilization of calcium alginate [3], [11], [12], [17]. The schematic of the initial preparation of eggshells and tea waste immobilized with calcium alginate as the bbiosorbentis presented in Figure 1, step 1. The eggshell and tea waste powder, which resulted from the pre-processing, was activated using an H_2SO_4 solution as a bbiosorbent The eggshell and tea waste activation process for the biosorbent is shown in Figure 1, step 2. After the biosorbent activation, the immobilization process of the sodium alginate and $CaCl_2$ solution was carried out, as presented in Figure 1, step 3.

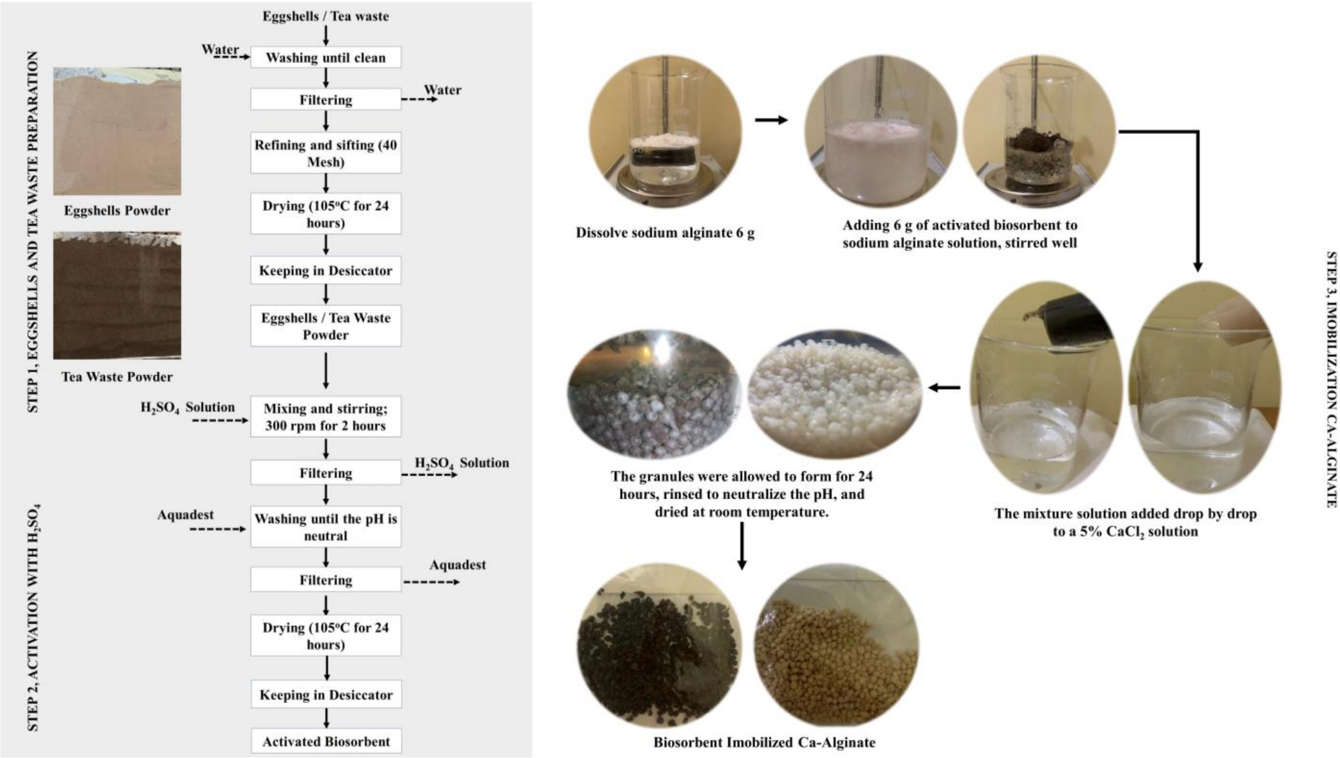

Figure 1 Schematic diagram of the preparation of a combination of bio sorbent by immobilized eggshells and tea waste in calcium alginate

2.3 Adsorption Experiments

To perform batch adsorption, the bio sorbent ratios between eggshells and tea waste were set as 2.67:12.33, 3.75:11.25, 7.5:7.5, 11.25:3.75, and 12.33:2.67, with the mass of the batik industry wastewater in a 250 mL Erlenmeyer flask. The pH solution was immediately adjusted using 0.1 N HCl and 0.1 N NaOH. After weighing, the bio sorbent was placed into the liquid waste and stirred using a magnetic stirrer. The moving process was Performed with time variations of 47.13, 50, 60, 70, and 72.87 min and a speed of 130 rpm. Furthermore, the samples were tested for COD levels referring to the Indonesian National Standard 6989.2-2019. The removal percentage of the COD level was calculated by Equation 1.

$$R\ (\%) = (Co - Ce) \times 100/Co \quad \text{(Equation 1)}$$

Where:
R is the removal rate of the COD,
Co is the initial COD concentration (mg L−1) in the batik wastewater before the adsorption process, and
Ce is the residual COD concentration (mg L−1) after the adsorption process.

2.4 Response Surface Methodology Design

The response response surface experiments by applying the alpha's central composite design (CCD) for orthogonality (Statistica 10.0 Statistical Software, Hamburg, Germany). The response surface methodology (RSM) also used the response surface methodology (RSM) approach to observe the bio-sorbent ratio, contact time, and pH effect on the bio-sorbent COD absorption. Table 1 illustrates the independent variables for CCD trials.

2.5 Fourier Transform Infrared Analysis

Fourier Transform Infrared (FTIR) analysis was performed following the SOP for the PerkinElmer Spectrum IR 10.6.1 and in the wavenumber range of 4000 cm^{-1} to 400 cm^{-1}. The resulting spectrum was analyzed using Perkin Elmer's FTIR Spectrum software.

2.6 Scanning Electron Microscopy–Energy Dispersive X-Ray Analysis

A microstructure analysis with scanning electron microscopy (SEM) was performed using the SEM–energy dispersive x-ray (EDX) JEOL JSM-6510LA device. SEM was operated with the following standard operating parameters high voltage of 20 kV, the spot size of 30, work distance of 10 mm, and SEM magnification at 3000×, 5000×, and 10000× scales. It performed this analysis on the bio sorbent before and after being used in the adsorption process. This analysis compared the activated carbon surfaces based on the SEM micrograph images.

2.7 Statistical Analysis

At this stage, it used empirical statistical techniques for the regression analysis using statistical applications if the final level of the COD in the batik industrial wastewater is known. Next, the RSM response surface on the effect of the contact time and ratio of the material to the final COD content was calculated. Then, the pH and contact time outcome on the final COD content and the effect of pH and material ratio on the final COD content was calculated.

Table 1 Independent variables in the central composite design statistical experimental design

Independent variables	Star low	Low point	Center point	High point	Star high
Ratio of biosorbent (g)	2.67:12.33	3.75:11.25	7.5:7.5	11.25:3.75	12,33:2,67
Contact time (minute)	47,13	50	60	70	72,87
pH sample	1,71	2	3	4	4,28

3 Results and Discussion

3.1 FTIR Analysis

Several studies on the FTIR analysis of the eggshell bio sorbent [18], [19] and tea waste bio sorbent [20], [21] have been performed to obtain information on the functional groups contained in the materials. The FTIR characterization of Ca-alginate-immobilized eggshell biosorbent is presented in Figure 2. Figure 3 shows the FTIR characterization of the Ca-alginate-immobilized tea waste biosorbent.

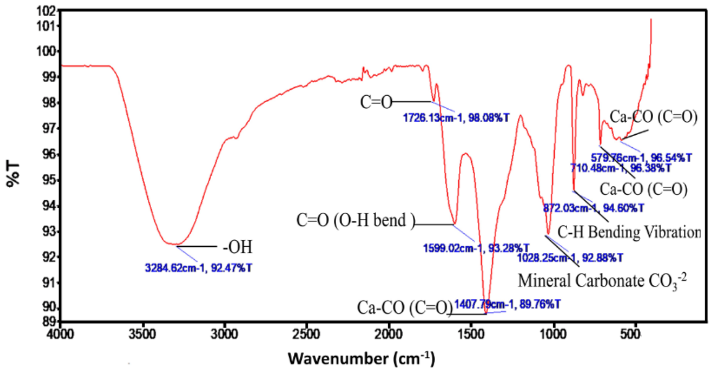

Figure 2 FTIR spectrum of the Ca-alginate immobilized eggshells biosorbent

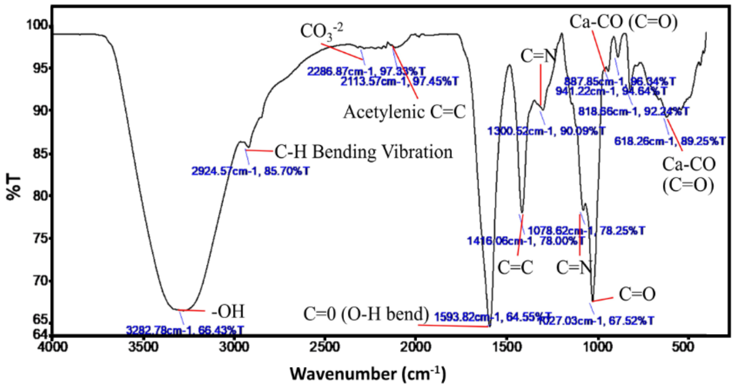

Figure 3 FTIR spectrum of the Ca-alginate immobilized tea waste biosorbent

The results of this study are in line with those of research by [18] and [20]. The peaks of $CaCO_3$, carbonate minerals, amines, O–H, C–O, and C=O groups indicate that the resulting Ca-alginate-immobilized eggshells and Ca-alginate-immobilized tea waste bio sorbents tend to be polar. By contrast, the biosorbent of substances that tend to be polar has a vital role in the adsorption process because of the large area in the results of the FTIR analysis. The peaks of alginate showed the presence of alginate compounds, as evidenced by the numbers 15599.02 and 872.03 cm^{-1} in the eggshell biosorbent and 1593.82 and 818.66 cm^{-1} in the tea waste biosorbent.

3.2 SEM Analysis

Figures 4 and 5 present the results of the bio sorbent characterization of the Ca-alginate-immobilized eggshell and tea waste before and after the adsorption of COD levels in the batik industrial wastewater. Figure 4(a) shows the morphology of the Ca-alginate-immobilized eggshell bio sorbent before the COD absorption process. The sample morphology includes porous particles in an alginate interpenetration network. These clumps indicate that the bio sorbent contains protein fibres and CaCO3. Figure 5(a) shows the morphology of the Ca-alginate-immobilized tea waste bio sorbent before the COD absorption process. The sample is a porous, nearly spherical particle in an interpenetrated alginate network. The immobilized bio sorbent forms a bio sorbent network trapped in the Ca-alginate polymer matrix, which is abundant and has a large surface area. This study's results align with those of the research by [12] and [22].

Figures 4 (b) and 5(b) show that the bio sorbent surface has many irregular lumps, and Figures 4(b) and 5(b) show that the surface of the bio sorbent has many irregular lumps. The pores of the bio sorbents are not visible in Figures 4 and 5. The COD molecules have closed the pores of the bio sorbent, lowering the COD levels in the batik industrial wastewater.

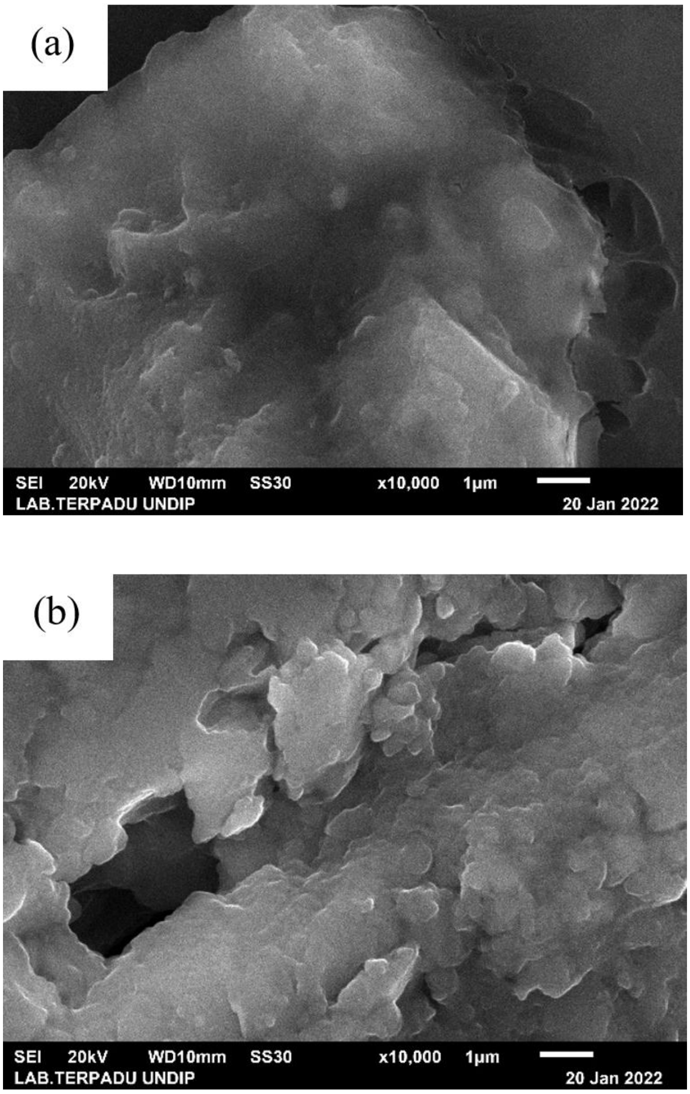

Figure 4 Results of the SEM Analysis of the Ca-alginate immobilized eggshells biosorbent (a) bio sorbent eggshells before the COD absorption process, (b) bio sorbent after the COD absorption process

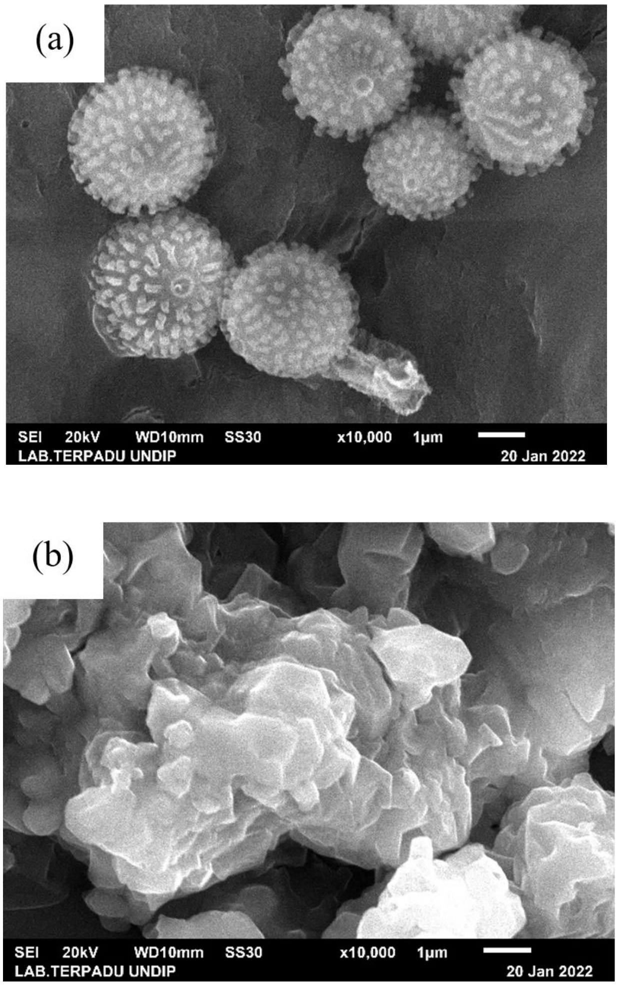

Figure 5 Results of the SEM Analysis the Ca-alginate immobilized tea waste biosorbent (a) bio sorbent tea waste before the COD absorption process, (b) bio sorbent tea waste after the COD absorption process

3.3 EDX Analysis

Tables 2 and 3 show EDX analysis results on the Ca-alginate-immobilized eggshell and tea waste bio sorbents after the absorption process of COD levels. The chemical components contained in the eggshell bio sorbent and Ca-alginate-immobilized tea waste had the highest COD content after the absorption process. Namely, element O, compared to the contents of C and Ca. The high carbon content is attributed to the activation process, which removes other impurities in the bio sorbent. The highest O content is attributed to the activation temperature, where the higher the temperature, the more the decomposition reaction of $CaCO_3$ and CaO by releasing CO_2. The components of Na and Cl indicate the element of Ca-alginate in the bio sorbent.

Table 2 EDX analysis on the Ca-alginate-immobilized eggshell biosorbent after the absorption process of COD levels

Element	(keV)	Mass%	Sigma	Atom%	K
C K	0.277	39.56	0.26	48.80	26.3129
N K	0.392	5.57	0.27	5.89	5.7579
O K	0.525	42.61	0.44	39.46	45.1972
Na K	1.041	3.13	0.06	2.02	4.1062
S K	2.307	4.88	0.05	2.26	9.8183
Cl K	2.621	0.19	0.01	0.08	0.4183
Ca K	3.690	4.05	0.06	1.50	8.3892
Total		100		100	

Table 3 EDX analysis on the Calcium alginate immobilized tea waste biosorbent after the absorption process of COD levels

Element	(keV)	Mass%	Sigma	Atom%	K
C K	0.277	35.33	0.24	46.04	18.7175
O K	0.525	47.62	0.41	46.58	49.3271
Na K	1.041	0.68	0.03	0.47	0.8070
S K	2.307	7.08	0.06	3.45	13.3396
Ca K	3.690	8.53	0.07	3.33	16.5413
Zr L	2.042	0.75	0.04	0.13	1.2675
Total		100		100	

3.4 Parameter Effect on the COD Level in the Batik Industrial Wastewater

The running parameters were considered through 16 experiments using independent variables of bio-sorbent ratio, contact time, and pH on the bio-sorbent COD absorption. The sixteen experiments on the responses of the removal of COD levels in the batik industry water waste by bio sorbents are described in Table 5. Using the collected data, it can analyze variance (ANOVA) and surface plots to determine the percentage reduction in the COD levels in the batik wastewater. The ANOVA results are described in Table 5. and surface plots are presented in Figure 6.

In Figure 6, the most optimum part (most per cent decrease in the COD levels) is marked on the left end of the highest curve sheet, with a material ratio of 2–3 g and contact time of 54–60 min. The higher the bio sorbent material ratio, the lower the COD in the batik liquid waste produced. The contact time should be between 54 and 62 min. If it is longer, the percentage reduction in COD levels will be more minor, even if the effect is statistically insignificant. A material ratio of 2–3 grams and a pH of 2–3.1 indicate the most optimum part (the most significant per cent decrease in the COD content). The lower the pH and the higher the ratio of the bio sorbent, the lower the percentage decrease in the COD levels. The most optimal part (per cent decrease in the COD levels) is the contact time of 54–62 min, and the pH of the sample is 2–3. The contact time is best between 54–62 min. If it is longer than 62 min, the percentage decrease in the COD levels is minor but still significant. Hence, the lower the pH, the lower the COD reduction percentage.

In the ANOVA table in the linear section, the P-value for the bio sorbent material ratio and the sample pH are 0.002057 and 0.020213, respectively, which are smaller than $\alpha = 0.05$. Hence, the bio sorbent material's variable ratio significantly affects the percentage reduction in COD levels in the batik industry wastewater. The contact time P-value is 0.090441, which is greater than 0.05, indicating that the contact time has no significant effect on the percentage reduction in COD levels in the batik wastewater. The F value of the fisher's test on the bio sorbent material ratio was 28.81767, the contact time was 5.02574, and the pH of the sample was 9.82401.

A critical value was used to determine the optimal conditions for reducing the COD levels in the batik wastewater. Table 7 shows the crucial importance of the optimization condition of the percentage reduction in the batik industry wastewater COD levels achieved when the material ratio is 2.67:0.52065, the contact time is 58.05245 min, and the sample pH is 2.59344.

Table 4 Tabulation data on the removal of COD levels in the batik industry water waste by the biosorbent

Ratio of the biosorbent (g)	Contact time (minute)	pH sample	Removal of the COD levels (%)
3.75	50	2	86
3.75	50	4	85
3.75	70	2	86
3.75	70	4	83
11.25	50	2	82
11.25	50	4	78
11.25	70	2	78
11.25	70	4	77
2.67	60	3	89
12.33	60	3	82
7.5	47.13	3	87
7.5	72.87	3	81
7.5	60	1.71	88
7.5	60	4.29	79
7.5	60	3	86
7.5	60	3	86

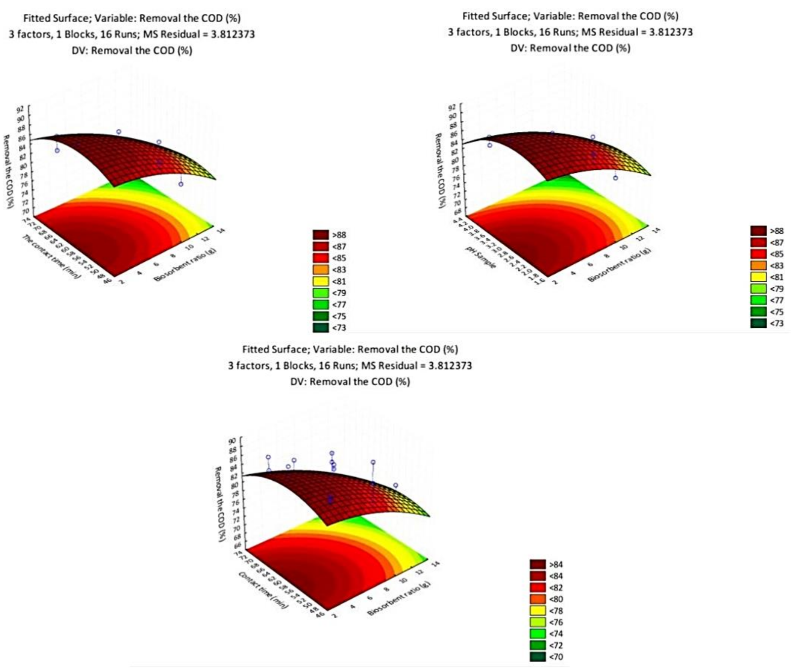

Figure 6 Surface plot of the effect of independent variables on the percentage of COD levels in the batik industrial wastewater

Table 5 ANOVA results for the removal of the COD levels (%)

Factor	ANOVA; Var.: Removal of the COD levels (%); R-sqr = 0.89763; Adj:0.74406 3 factors, 1 Blocks, 16 Runs; MS Residual = 3.812373 DV: Removal of the COD levels (%)				
	SS	df	MS	F	P
(1) Ratio of biosorbent (g) (L)	102.2390	1	102.2390	26.81767	0.002057
Ratio of biosorbent (g) (Q)	3.2918	1	3.2918	0.86346	0.388627
(2) Contact time (minute) (L)	19.1600	1	19.1600	5.02574	0.066182
Contact time (minute) (Q)	15.4894	1	15.4894	4.06294	0.090441
(3) pH Sample (L)	37.4528	1	37.4528	9.82401	0.020213
pH Sample (Q)	21.5553	1	21.5553	5.65404	0.054931
1L by 2 L	1.1250	1	1.1250	0.29509	0.606552
1L by 3L	0.1250	1	0.1250	0.03279	0.862271
2L by 3 L	0.1250	1	0.1250	0.03279	0.862271
Error	22.8742	6	3.8124		
Total SS	223.4375	15			

Table 6 Responses of the quadratic polynomial model equations

Response	Quadratic polynomial model equations
Ratio of biosorbent (g) with contact time (minute)	$Z = 21.330 + 0.724x - 0.055x^2 + 1.923y - 0.017y^2 - 0.010xy - 0.0333 \times 3x + 0.0125y + 10.874$
Ratio of biosorbent (g) with pH sample	$Z = 21.330 + 0.724x - 0.055x^2 + 9.569y - 1.981y^2 - 0.010 \times 60x - 0.033xy + 0.013 \times 60y + 54.909$
Contact time (minute) with pH sample	$Z = 21.330 + 0.724x - 0.055x^2 + 1.923y - 0.017y^2 - 0.010xy - 0.033 \times 4x + 0.013 \times 4y + 6.574$

Table 7 Predicted value of the optimum COD level decrease in the batik water waste with the critical value of the material ratio, contact time, and pH

Factor	Critical Values; Variable: Removal of COD levels (%) Solution: Maximum Predicted value at solution: 89.74281		
	SS	df	MS
Ratio of the biosorbent (g)	2.67304	0.52065	12.32696
Contact time (minute)	47.12811	58.05245	72.87189
pH sample	1.71281	2.59344	4.28719

4 Conclusions

Biosorbents are solid substances that can absorb a fluid phase's absorption (adsorption). This study focused on using eggshells and tea dregs with an acid activation method mobilized by ca-alginate to reduce COD levels in waste left over from the liquid production of industrial batik. It chose the eggshell because it contains Calcium Carbonate ($CaCO_3$), a polar adsorbent because of its opposite nature & CaO has a hexagonal structure with an internal grid intertwined with H +, Na, and others. While it chose the pulp because it has a high cellulose content, it can be used as an adsorbent to absorb metals in polluted water to improve the quality of the water that produces both physical and chemical properties. With the entrapment method by utilizing ca-alginate, it is hoped that bio sorbents have advantages, including having mechanical strength, can form strong aggregates, rigidity, size and porosity characteristics.

Based on the results, it obtained the percentage of decrease in COD levels in batik industry liquid waste under operating conditions. The ratio of eggshell material: to tea dregs was 2.67: 12.33, the contact time was 60 minutes, and the sample pH was 3, with a percentage decrease in COD levels in batik industry liquid waste by 89%.

Research on bio sorbents with a combination of ca-alginate mobilized materials needs to be carried out to increase the percentage of cod levels in batik industry liquid waste by using other activation processes to get a higher rate of COD levels of batik industry liquid waste and the need to be studied regarding further bio sorbent regeneration.

5 Declarations

5.1 Acknowledgments

The authors thank the UPT Laboratorium Terpadu Diponegoro University and BBTKLPP Yogyakarta for helping analyse this study.

5.2 Author Contributions

The names of the authors listed in this journal contributed to this research.

5.3 Funding Statement

This research was not supported by any funding sources.

5.4 Conflicts of Interest

The authors declare no conflict of interest.

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