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Biopolymer Composite Beads of Calcium Alginate-Fly Ash for Efficient Adsorption of Rhodamin B Dye

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Wastewater from anthropogenic activities such as the textile, dyeing and finishing industries release heavy metals that cause pollution of the environment, particularly the water resources and soil. Rhodamin B is one type of dye used in industries such as textile industry. In this research, we reported the results of designing the Calcium Alginate-Fly Ash (Biopolymer Composite Beads) and its application as an adsorbent to reduce the amount of Rhodamin B in wastewater. Calcium Alginate-Fly Ash composite beads were obtained by mixing sodium alginate with fly ash in distillate water then drop the solution in Calcium Chloride ($CaCl_2$) solution for shaping the beads. Calcium Alginate-Fly Ash characterization from the result of FTIR analysis showed the presence of OH functional group, carboxyl groups, and silica groups. The adsorption of Rhodamin B dye using composite beads was performed at various change in contact time with the different type of adsorbents (Calcium Alginate beads and Calcium Alginate-Fly Ash beads). The result showed that the highest reduction in Rhodamin B occurred at the contact time of 150 minutes with removal percentage 13.22% using Calcium Alginate-Fly Ash composite beads as adsorbent.

Keywords: Biopolymer; calcium alginate; Rhodamin B Dye

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Wastewater from anthropogenic activities such as the textile, dyeing, and finishing industries release heavy metals that cause pollution of the environment, particularly the water resources and soil [1]. Rhodamin B is one type of dye used in industries such as textile industry. It contains amino that is alkali and also benzene, so it can change the pH of water if excessively release into the environment. The contamination of Rhodamin B in water is a serious problem for the environment because of the difficulty in natural degradation by microorganism [2]. Those can disturb the life of water microorganisms and animals. Moreover, Rhodamin B which accumulates in the human body will cause serious problems such as poisoning, heart cancer, respiratory tract irritation, skin irritation and digestive tract irritation [3].

Some of the methods for declining dye waste are ion exchange, photocatalytic degradation, coagulation, ultrafiltration, biological processes, membrane separation, nanofiltration, adsorption, etc. Among those methods, adsorption is regarded as the most favorable due to its ease, cost-effectiveness, great efficiency, only produce few by-products and can be regenerated [4-6]. Textile industrial waste treatment often uses adsorbents such as activated carbon and chitosan [7]. However, those adsorbents have inadequate adsorption capacity.

Fly ash as one type of adsorbent using in adsorption process is a very fine particles that is released as a waste from the burning of used coal. A large number of fly ash from the burning of used coal in thermal power plants or combustion facilities needs final disposal. Therefore, the research for utilize fly ash has increased in the last two decades because it has been identified as appropriate adsorbent for heavy metals adsorption in wastewater [8]. Fly ash contains of silica oxide, alumina oxide, and iron oxide, which are good for the adsorption of heavy metal [9]. Fly ash has been used as an inexpensive adsorbent for water cleaning, heavy metal and dye adsorption.

The usage of fly ash as an adsorbent has difficulty in separating the process with wastewater and the requirement of special technology for its purification using air. Those problems are caused by the size of fly ash which is relatively small. Therefore, we need to find a solution for making it easy in the adsorption process.

Recently, there are numerous studies for economical and more effective adsorbents using natural polymers. Biopolymer as an adsorbent in removing heavy metal ions is a preferred alternative to chemical adsorbents. The use of polysaccharide derivatives can be an economical procedure in the

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adsorption process of water decontamination. Alginate as one of the polysaccharide biopolymers has a highly complex formation ability with numerous heavy metals. Sodium alginate is a biodegradable, non-toxic and hydrophilic polymer that is appropriate for the adsorption of toxicants in the water [10]. Therefore, it was selected as the material for the carrier matrix.

In this research, composite adsorbents were made from sodium alginate combined with fly ash for removing the heavy metal. Moreover, the beads that are produced will make it easier for separating adsorbents with wastewater.

MATERIALS AND METHODS

Materials and Equipment

Sodium alginate (Na-Alginate) was obtained from HiMedia. The fly ash obtained from Steel Plant in West Java was screened until 89 micron of particle size. The equipment needed for this research are 150 mesh sieve, beaker glass, measuring glass, volumetric pipet, magnetic stirrer, oven, analytic scales, cuvette and spectrophotometric.

Beads Preparation

The preparation step of Calcium Alginate-Fly Ash composite beads was conducted with the method of transfer ion between Na-Alginate-Fly Ash and Calcium chloride ($CaCl_2$). The first step, dissolved Na-Alginate (1 % w/v) in 100 mL distilled water then followed by the addition of 0.6 g fly ash while stirred until the solution completely mixed. Hereafter, the solution of Na-Alginate-Fly Ash with the help of a syringe was dripped into 0.1 M $CaCl_2$ solution with volume 100 mL until it formed beads. For the hardening process, the formed beads were left in $CaCl_2$ solution for 24 hours. After that the beads were filtered and washed thrice with distilled water before they were stored. The beads can be stored in distilled water at room temperature and the swollen beads were washed again three times with distilled water before we use them.

FTIR Analysis of Calcium Alginate-Fly Ash

The availability of functional groups in Calcium Alginate-Fly Ash composite bead was characterized using FTIR Spectrophotometer ATR. The FTIR analysis was conducted in wavelength range of 4000–400 cm^{-1}.

The Maximum Wavelength and the Calibration Curve for Rhodamin B

We need to determine the maximum wavelength of Rhodamin B before performing the adsorption of Rhodamin B with composite beads as adsorbent. The determination of Rhodamin B maximum wavelength was carried out using the Dynamica Spectrophotometer UV-Vis DB-20R double beam in 500–600 nm of the wavelength range and 0–2 of the absorbance range with various concentrations of Rhodamin B solution.

Adsorption of Rhodamin B

The research was performed by varying the contact time and type of adsorbents (Calcium Alginate beads and Calcium Alginate-Fly Ash beads). The maximum wavelength of Rhodamin B was used for measuring the adsorption of Rhodamin B by adsorbents from composite beads. First step, 25 g adsorbent was mixed with 100 ml of 0.05 g/L Rhodamin B solution in 400 rpm of stirring speed to determine the optimum contact time. The contact time variations were 0, 30, 60, 90, 120, 150, 180, 210, 240, and 1440 min. The step above was applied in the adsorption of Rhodamin B with both adsorbents (Calcium Alginate beads and Calcium Alginate-Fly Ash beads).

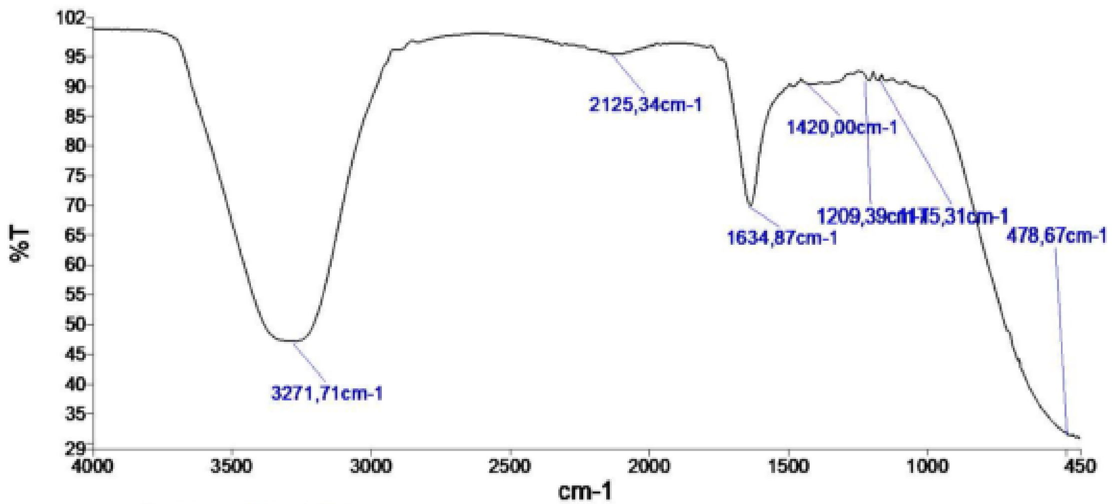

Figure 1. FTIR spectra of Calcium Alginate-Fly Ash.

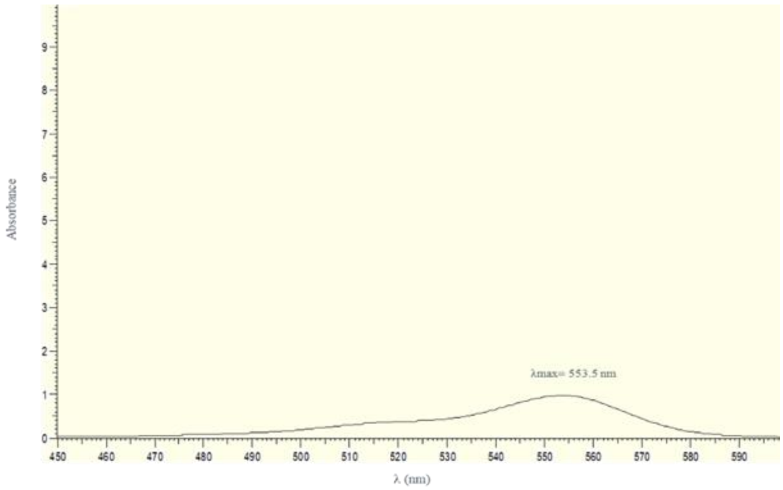

Figure 2. The maximum wavelength for Rhodamin B (λ_{max} = 553.5 nm).

After that the sample was tested with UV–Vis spectrophotometer to know the absorbance and also the concentration. Therefore, it could be used in determining the percent adsorption of Rhodamin B, which could be found by:

$$\text{Percentage of adsorption (\%)} = \frac{C_0 - C_t}{C_t} x100$$

Where C_0 is the concentration of Rhodamin B before the adsorption, and C_t is the concentration of Rhodamin B after the adsorption.

RESULTS AND DISCUSSIONS

Characterization of Calcium Alginate-Fly Ash Adsorbent using FTIR

The result of analyzing Calcium Alginate-Fly Ash adsorbent with FTIR shown in Figure 1. From the IR spectrum of Calcium Alginate-Fly Ash beads, the bands at 3271.71 cm^{-1} indicated the -OH group [11]. The adsorption peak of 1634.87 cm^{-1} and 1420 cm^{-1} assigned to the asymmetric and the symmetric of carboxyl (COO–) groups [12]. Peaks at 1175.31 cm^{-1} and 478.67 cm^{-1} indicate the asymmetric stretching bond of Si-O-Si and the vibration of the aluminum oxide from fly ash structure [13].

The Maximum Wavelength and the Calibration Curve of Rhodamin B

The maximum sensitivity of the samples containing Rhodamin B was provided by determining the maximum wavelength for Rhodamin B. The result showed that the maximum wavelength of Rhodamin B was 553.5 nm (Figure 2). The maximum wavelength was a bit different from the other study which was 558 nm [14].

From making the calibration curved, we obtained the linear regression equation. The equation would be used in discovering the absorbance of the adsorption sample and the correlation between the concentration of Rhodamin B and its absorbance. Figure 3 was shown the calibration curve of Rhodamin B with slope value of 0.01507, intercept value of 0.02941, and R^2 value of 0.99884. The R^2 value was close to 1, so the calibration curve could be categorized as good.

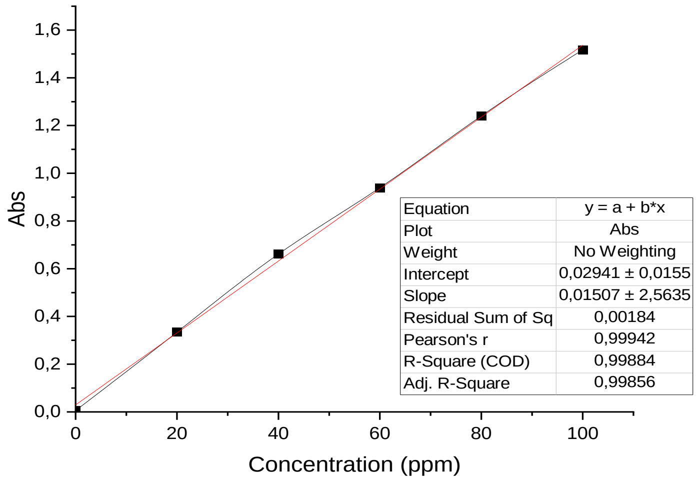

Figure 3. Calibration curve of Rhodamin B.

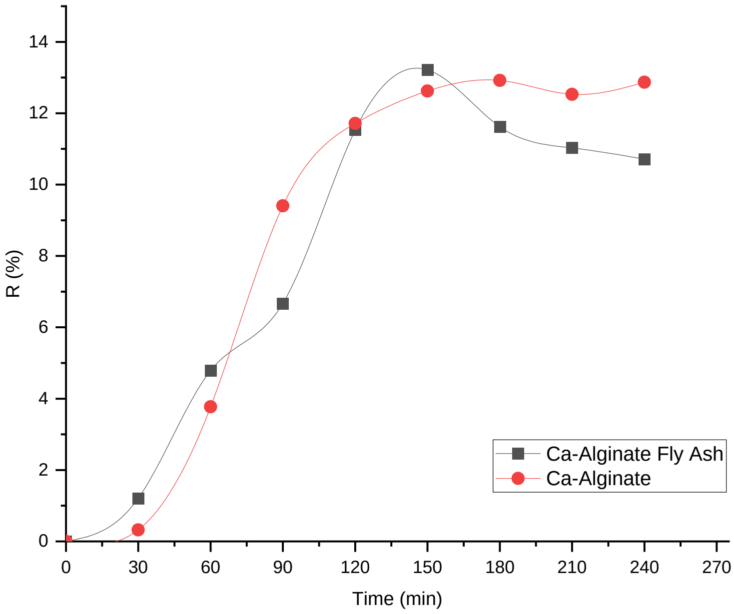

Figure 4. The result of various contact time on the adsorption of Rhodamin B by Calcium Alginate-Fly Ash beads and Calcium Alginate beads.

Determination of the Adsorbents and the Adsorption Optimum Contact Time of Rhodamin B

The result of the variation of contact time between the Calcium Alginate-Fly Ash adsorbent and Rhodamin B is shown in Figure 4.

In Figure. 4, it could be seen that the Calcium Alginate-Fly Ash adsorbent could adsorb 13.22% of Rhodamin B at 150 minutes contact time, while the Calcium Alginate adsorbent could adsorb 12.92% of Rhodamin B at 180 minutes. From those result, the ability of Calcium Alginate-Fly Ash beads in adsorbing Rhodamin B was higher than Ca-Alginate beads. This was because the addition of fly ash in Calcium Alginate beads increasing the surface area for adsorption. The adsorption percentage of Rhodamin B decreased at 180 minutes contact time when using Calcium Alginate-Fly Ash beads and at 210 minutes contact time when using Calcium Alginate beads. This was caused of the decreased amount of active sides because the adsorbent's surface were covered by dye solution layer. Thus decreasing also indicates the desorption process where the addition of contact time between the dye and the adsorbent will make the ions that have been adsorbed were re-released due to encountering saturation. Those was due to the adsorption that has reached an equilibrium [15]. The contact between the dye and the adsorbent that exceeded its optimum contact time, resulted in a greater amount of dye exchange, which showed the decreasing of absorption capacity [16]. The result also show that raw fly ash still has a low adsorption efficiency due to the presence of contaminants like tar and volatile materials, which cover the active surface and impede the adsorption process.

CONCLUSION

This research indicates that Calcium Alginate-Fly Ash composite beads could be used for removing Rhodamin B from wastewater. The Calcium Alginate-Fly Ash was characterized using FTIR that showed the presence of OH functional group, carboxyl groups and silica groups. The optimum condition for the adsorption of Rhodamin dye using Calcium Alginate-Fly Ash composite beads as adsorbent was obtained at contact time of 150 minutes with 13.22% removal percentage of Rhodamin B.

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