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Muhammad, Rafi
Department of Civil and Environmental Engineering, Universitas Indonesia

Adityosulindro, Sandyanto
Department of Civil and Environmental Engineering, Universitas Indonesia

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Biosorption of Brilliant Green Dye from Synthetic Wastewater by Modified Wild Algae Biomass

Rafi Muhammad[1], Sandyanto Adityosulindro[1,*]
[1]Department of Civil and Environmental Engineering, Universitas Indonesia, Indonesia

*Author to whom correspondence should be addressed:
E-mail: adityosulindro@eng.ui.ac.id

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Abstract: In this study, algae originating from Lake Agathis Universitas Indonesia was converted to biosorbent for removal of dye from water. The effectiveness of dye removal was evaluated using biomass (without activation) and biomass activated by HCl+TEOS and Soxhletation+H_2SO_4 methods. Brilliant green was used to simulate dye wastewater, and the biosorption assays were conducted in a laboratory batch system. The results showed that the adsorbent activated by Soxhletation+H_2SO_4 was the most effective (C_{pol} = 80 mg/L; C_{ads} = 0.5 g/L; 77% removal). Decolorization improved under alkaline pH, while high dye concentration and temperature showed the opposite effect. The adsorption isotherm and kinetic data fitted the Langmuir and the pseudo-second-order model, respectively.

Keywords: Adsorption, Biosorbent, Brilliant Green, Algae

1. Introduction

Industrial development is one of the positive indicators in the economy of a region or country. However, industrial activity tends to be directly proportional to wastewater generation. Industrial wastewater generally contains various contaminants such as solids, organic compounds, metals, pathogens that may be harmful to human and aquatic life[1,2)]. The textile industry is one of the main concerns considering the huge quantity of wastewater generated during the textile production[3)] and often directly discharge into the sewage, making the sunlight unable to enter the water bodies to be utilized by the water ecosystem[4)]. Furthermore, textile wastewater typically contains non-biodegradable substances[5)] expressed by high BOD and COD values. Lack of freshwater resources especially in developing countries (annual water withdrawals rose by up to 8% in developing countries)[6)] has created the technological intervention in tackling water pollution urgently needed due to the high demand for freshwater.

Among various dyes, Brilliant Green (BG) has been used in many textiles and non-textile industries such as tannery, leather, cosmetics, paper, and green colorant[7)]. BG is also used as a dermatological agent, veterinary medicine[8)] and aquaculture[9)]. However, brilliant green poses several potential toxicities to humans that will cause skin irritation, respiratory tract irritation, gastrointestinal irritation[10)], bladder cancer, and chromosome deviation in Mammalia[7)].

Dye contaminants in water can be removed by physical, chemical, or biological treatment. Biological treatments are usually cost-effective[11)], but they may not be effective since some dye compounds may inhibit some microbial activity[12)]. Chemical treatments are usually effective but high operational cost and may generate chemical sludge or more toxic by-products. Physical treatments are usually low-cost and versatile, but as a mass transfer process, they require further steps to process the concentrate[11)]. Among physical treatments, adsorption is a promising alternative considering its efficacy and simplicity. Aside from carbon active, several materials can also be used as adsorbent such as silica gel and zeolite that could be used even for cooling and desalination adsorption process [13)]. Currently, the research trend is towards the development of biosorbent[14)], waste-based[15)] and biomass-based adsorbents[16)].

The use of algae as biosorbent material has the advantage of good degradation ability, especially for azo dyes because it can break down azo compound groups into aromatic amine groups which are utilized by algae for metabolism[17)]. Utilization of algae can also be done either by using live algae or in the form of biomass. The use of dead algae (biomass) may overcome the problem of wastewater toxicity on live algae[18)] that has a fatal effect on both people and animals, in this case, could potentially be lethal. The presence of polysaccharides with acid functional groups, fucoidans, alginate's carboxyl groups, and amino groups plays a significant role in the adsorption of metals[19)], dyes[20)] and cationic compounds[21)]. However, several constraints are the potential organic leaching (especially when using brown algae) due to the abundance of organic compounds (lipids, carbohydrates, pigments, etc.)[22]. Those organic compounds could inevitably be leached and dissolved in the solution during reaction/adsorption. Therefore, the lipids extraction process (using Soxhlet extractor) is necessary to remove the organic compound. Other shortcomings of algae's utilization are low specific gravity, small size, potentially damaged by other microorganisms through degradation process, and not possible to directly used in the adsorption column since it is not granular and very soft[20]. Thus, an immobilization method should be applied by reacting supporting polymers such as silica to the biomass (sol-gel process).

Much research using algae-based biosorbent has been conducted by far. Buhani, Hariyanti, et al., (2019)[21] and Buhani, Suharso, et al., (2019)[20] found that the immobilizing method combined with HCl has increased the removal efficiency to 20-75% and can be reused for 4 repetitions. Shao et al., (2017)[22] showed that activating the biomass using soxhletation and mixing it with H_2SO_4 96% will increase the adsorption capacity from 416 mg/g (non-activated biomass) to 526 mg/g and able to remove 98.9% dye concentration from the solution by using 0.6 g/L of biomass[22]. Maisarah et al., (2021)[23] reported that the algae-based biomass activated by the NaOH can remove Zinc up to 92% in 120 minutes[23].

In this work, biomass prepared from wild algae is used to remove Brilliant Green dye from water. Comparison of some activation methods, characterization of selected algae-biomass and adsorption operating parameters were carried out.

2. Material and Method

Two methods of activation were used in this study including HCl+TEOS[20,21], and Soxhletation+H_2SO_4[22]. First, algae were taken from Lake Agathis of Universitas Indonesia using plankton net[24], cleaned using distilled water then dried using Memmert UFB 50 oven in 105°C overnight. Biomass ground using pestle and mortar to a size of 60 mesh. For the HCl+TEOS activation method, 0.4 g biomass was used. The preparation was carried out according to the research Buhani, Hariyanti, et al., (2019)[21] and Buhani, Suharso, et al., (2019)[20], 5 ml TEOS mixed with 2.5 ml distilled water and stirred for 30 minutes (named TEOS solution). After that, the solution's pH was adjusted by adding HCl 1M. In another beaker glass, 0.4 g of biomass were mixed with 5 ml of ethanol for 30 minutes (named biomass solution). The TEOS solution and biomass solution were mixed and stirred for 24 hours (150 rpm). The formed gel was then sieved using filtration paper, allowed to stand for 24 hours, and washed by 60:40 solution of distilled water and ethanol mixture to neutralize the gel's pH. This biosorbent is named Algae Silica hybrid (AS).

For the Soxhletation+H_2SO_4 activation method, 5-10 g of biomass was used. The preparation method was carried out according to the research conducted by Shao et al., (2017)[22]. The high presence of organic substances (lipids, protein, carbohydrates, etc.) in the biomass will lead to a potential leaching phenomenon when the biosorption process happens. Hence the extraction of lipids should be conducted using the sohxletation method and n-hexane as the solvent (called DAB, Defatted Algae Biomass). The DAB (5 g) was then mixed with 30 ml of H_2SO_4 96% for 24 hours (373K). After 24 hours, the solution's pH was neutralized by using $NaHCO_3$ 2% and the solids (DAB-S) were separated from the solution through sedimentation process (1-2 days). The DAB-S was then dried using an oven (105°C) overnight and neutralized its pH value by washing it using distilled water. The DAB-S dried again and ground to a size of 100-150 μm.

Moreover, to identify the dye concentration in the solution, a calibration curve is used. Calibration curve was created by reading the absorbance value of 0 mg/L, 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L, 10 mg/L dye concentration. Using the absorbance value, a dye concentration and absorbance relationship curve was created and obtained a linear equation will be used to convert the absorbance value of the later experiment to dye concentration.

The experiment was conducted by reacting dye with a biosorbent according to the prescribed dose. The experiment to identify the biosorption process was conducted through the batch method by reacting 100 ml of desired concentration of brilliant green dye solution (except in the study of contact time effect used 500 ml of solution) with the desired amount of biosorbent. The solution was mixed at 300 rpm. To determine the effect of operational parameters, variations were made on the biosorbent concentration (0.125 g/L, 0.25 g/L, 0.3 g/L, 0.4 g/L, 0.5 g/L, 1 g/L), dye concentration (40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L, 160 mg/L), solution's pH value (2, 3.6, 8), and solution's temperature (30°C and 60°C).

3. Results

3.1 Selection of Biosorbent

The determination of biosorbent was considered based on technical (removal efficiency). To assess the removal efficiency, a 100 ml solution of Brilliant Green with 80 mg/L of concentration was created and 1 g/L of biosorbent was added to the solution and mixed for 120 minutes (300 rpm). There were four biosorbent assessed in this experiment, which were Biomass, AS, DAB, and DAB-S.

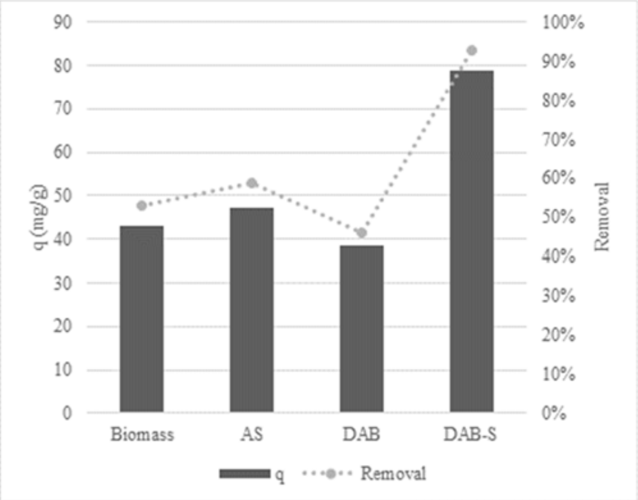

Fig. 1: Effect of Biosorbent Activation Method

The result presented in Fig. 1 states that the activation method plays a significant role in removing the pollutant. The DAB-S could remove 93% of pollutants due to the binding site's abundance as the result of the lipid extraction and the abundance of OH^- functional groups on its surface as the result of the reaction with H_2SO_4 that plays a big role in enhancing the adsorption capacity to 78.9 mg/g from 38.4 mg/g (DAB). According to the result, the DAB-S was selected.

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3.2 Biosorbent Characterizations

The characterization of the selected biosorbent was conducted through surface morphological and surface elements identification (SEM-EDX), average pore size and volume (BET), and functional groups identification (FTIR). Through SEM, it was identified that the activation method has changed the surface's morphological of biomass became more granular than before the biomass was activated (smooth surface). This condition will increase the surface area and surface porosity. The surface elements were identified through the EDX method, the result shows that carbon (27.8%) was the dominant element followed by oxygen (44.89) and silica (11.22%) in biomass (before activated). However, the domination of carbon was replaced by silica (34.07%). The presence of silica could happen due to several reasons such as its habitat and has a close relationship with the classification of soil/sediment, which clay have an abundance of Al_2SiO_5[25]. Naturally, algae have the ability to absorb non-essential nutrients and keep them in their cell wall [26], hence the presence of silica could happen due to algae's natural behavior. Moreover, the presence of silica is an advantage for cationic dye adsorption[27].

Through the BET method, the average pore size value of DAB-S is 189.6 m^2/g with the pore volume value is 0.2598 cc/g and the average pore size is 31.2 Å (3.12 nm). According to IUPAC, the pore size value of DAB-S was categorized as mesoporous biosorbent since it was between the range of 2-50 nm of size [20]. According to Gómez et al., (2014)[28], an ideal biosorbent should have a vast surface area, high pore volume that can be entered by the pollutant's molecule, and easily treated to regenerate. Since dye molecules are considered bulk molecules, hence mesoporous biosorbent will be the suitable ones to remove the pollutant due to their large pore size.

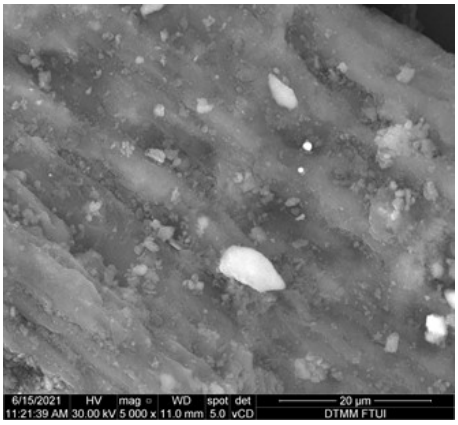

Fig. 2: SEM result of Biomass with 5000x Enhancement

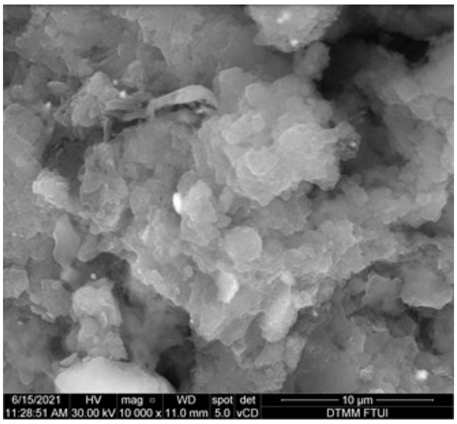

Fig. 3: SEM result DAB-S with 5000x Enhancement

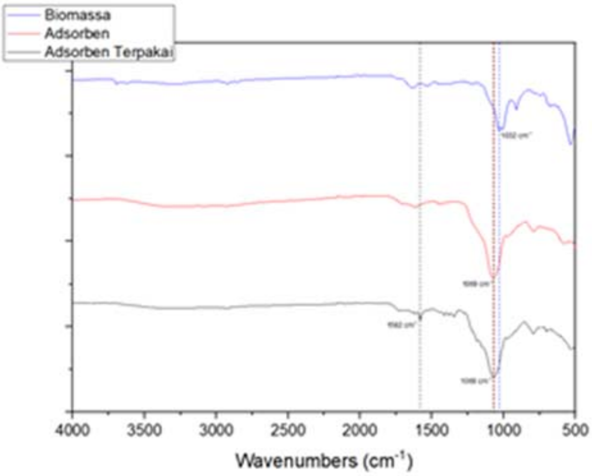

Fig. 4: FTIR Result

Identification of surface's functional group conducted through FTIR and discovered that peak value at 1032 cm^{-1} in biomass was related to C─O and was replaced by 1069 cm-1 (S=O) after the biomass is activated. Furthermore, the same peak value was reappeared in used DAB-S with the appearance of another peak in 1582 cm^{-1} which related to the C=C functional group. The appearance of C=C due to the interaction between pollutant molecules and binding sites which was increased the biosorbent's carbon content due to the bonding of the C atom in the pollutant molecule with the C atom at the binding site. This condition was similar to the reappearance phenomenon that occurred in [22] research due to the interaction between the pollutant's molecule and the surface of the biosorbent.

3.3 Reaction Time Determination and Effect of Contact Time

The reaction time of the experiment was determined by identifying the highest removal and identifying the equilibrium time. The study was conducted using 500 ml of 80 mg/L dye and 0.5 g/L biosorbent that agitated in 120 minutes. The result shows that the rapid absorption process happens at the first 5 minutes of reaction and steadily increases until reaching the 120 minutes (125 mg/g) of the reaction and gradually decreases until reaching the 180th minute (102 mg/g). This condition could happen due to the saturated active binding site [21,22]. Moreover, the abundance of the active binding sites has allowed the rapid adsorption phenomenon in the first 5 minutes of reaction [22]. However, the removal efficiency is decreasing after 120 minutes of reaction due to several conditions such as the migration of contaminant ions into the biosorbent's interior[29] and the repulsive force between adsorbate and pollutants in the water that happens when the active binding site is saturated. Hence, according to the experiment's result, it can be concluded that 120 minutes will be the optimum time for the reaction.

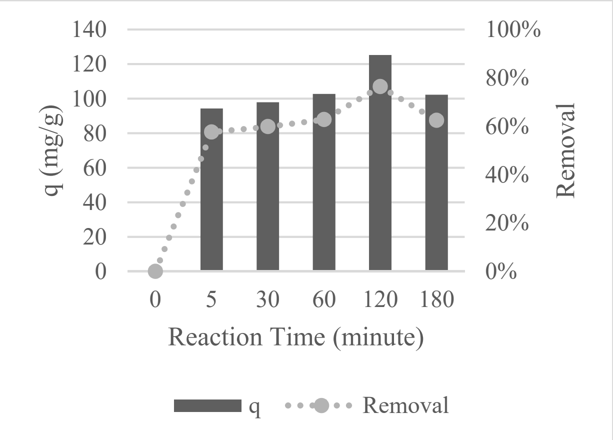

Fig. 5: Effect of Reaction Time

3.4 Effect of Biosorbent Dosage

The effect of biosorbent dosage plays a significant role in the process of absorption. The study was conducted by reacting 100 ml of 80 mg/L dye and the biosorbent dosage was varied namely 0.125 g/L, 0.25 g/L, 0.3 g/L, 0.4 g/L, 0.5 g/L, 1 g/L that reacted for 120 minutes. The highest removal efficiency occurs in 1 g/L of biosorbent (93%). Generally, removal efficiency will increase with increasing adsorbent dose[22] due to the increased surface area of adsorption. Considering economical and operational considerations, the 0.5 g/L of biosorbent dose is selected for further assays.

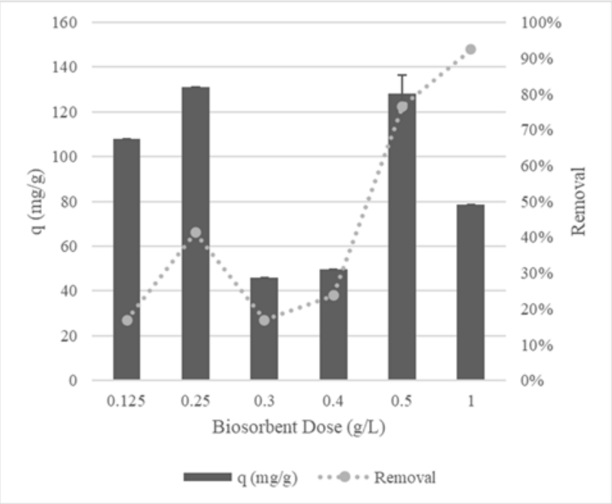

Fig. 6: Effect of Biosorbent Dose

3.5 Effect of Pollutant Concentration

The initial dye concentration plays a significant role, the higher it is, the lower removal efficiency will occur. The experiment was conducted by reacting 100 ml of 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L, 160 mg/L of dye and 0.5 g/L of biosorbent dose were mixed for 120 minutes. The result shows that the highest removal efficiency occurs in 80 mg/L of dye (77%, 128.33 mg/g). The result also shows that the removal efficiency is decreased along with the increasing pollutant concentration due to the saturated active binding site by the adsorbed pollutant that resulted in an insignificant amount of adsorption[30]. Moreover, the adsorption capacity also decreases when the dye concentration increased. This condition happened due to repulsive force between adsorbate and pollutant in the water that happens when the active binding site is saturated and also between adsorbate and causes the reverse adsorption phenomenon[28]. This condition also contributes to decreasing of adsorption capacity value especially due to the distance between the molecules that have been adsorbed to be far apart due to the phenomenon of repulsion between the adsorbed molecules.

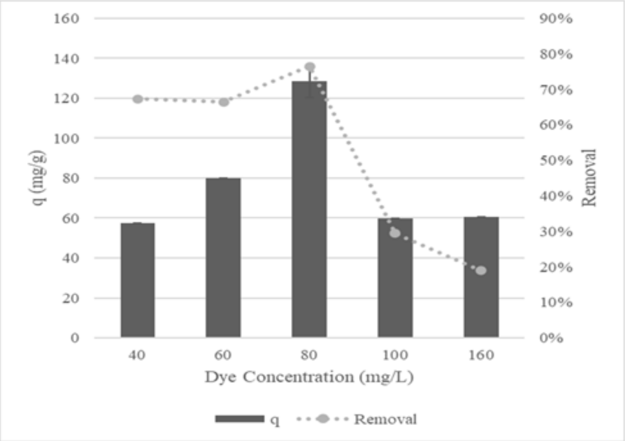

Fig. 7: Effect of Dye Concentration

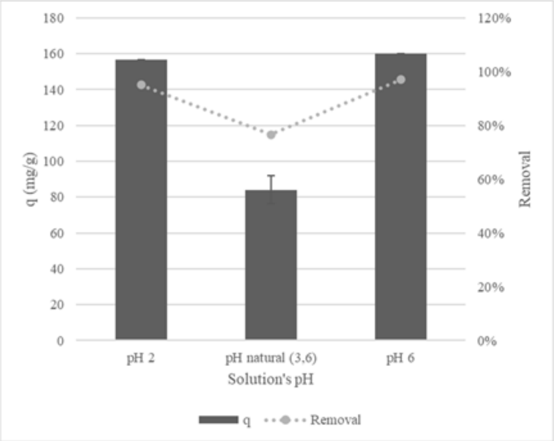

Fig. 8: Effect of Solution's pH

3.6 Effect of Solution's pH

The experiment to study the effect of the solution's pH was conducted by reacting 100 ml of 80 mg/L dye with 0.5 g/L biosorbent that was stirred for 120 minutes. Based on these data (Fig.8), the highest removal value is in the condition of the solution with a pH of 6, namely with an adsorption capacity of 159.94 mg/g and a removal efficiency value of 97%. The results obtained are per the research conducted by[31)] that states the higher the pH value, the higher the adsorption ability of the biosorbent, especially in removing cationic metals and basic dye group. According to to Yagub et al., (2014)[30)], the pH value affects the variation in the degree of ionization of the adsorbent molecule and the surface properties of the adsorbent. At a low pH value, the surface of the adsorbent experiences a protonation phenomenon caused by H^+ ions that cause an unideal removal process, especially for positively charged pollutants. The phenomenon of protonation that occurs is a condition where the surface of the adsorbent becomes positively charged due to the abundance of H^+ ions, this condition then results in the surface of the adsorbent not being ideal for the removal of cationic pollutants due to the large surface area of the adsorbent that positively charged. However, the result of this experiment also shows that high removal efficiency and adsorption capacity also occurs in lower pH value. This can occur due to the oxidation process of the adsorbent during the activation stage of algae biomass using 96% H_2SO_4[22)]. The activation process then changes the surface structure of the biomass to allow the adsorption process for cationic pollutants to occur optimally at a low pH. On the surface of algae, there are various types of compounds such as cellulose, alginic acid, amino acids, polymers of mannuronic acid and guluronic acid, metal salts (Na, Mg, Ca), to sulfated polysaccharides. In acidic solution conditions, the NH_2 group in the amino acid compound will bind with Cl^- forming an anionic surface condition so that it can bind cationic pollutants [32)].

3.7 Effect of Solution's Temperature

In this experiment, two variations of temperature were used, namely, 30ºC which represents room temperature, and 60ºC to determine the effect of two different solution temperature conditions. Several types of research, such as [8,19)], shows that the increase of the solution's temperature will reduce the adsorption capacity and removal efficiency of the adsorbent especially for adsorption of basic dye since the molecule and active binding site interaction in lower temperature will be dominated by exothermic static interaction and in higher temperature the endothermic hydrophobic interaction will be dominated and also the loss of the property of adsorbent happens in higher temperature resulting in a decrease in removal efficiency and adsorption capacity. Therefore, the experiment was carried out by reacting the biosorbent only in two variations of temperature since the result of similar research shows that higher temperature will decrease the adsorption capacity. The result shows that at a solution temperature of 30ºC, a more optimum removal process occurs which is indicated by an efficiency value of 73% and an adsorption capacity value of 128.33 mg/g. This is close to the previous study[31)] that temperature plays role in influencing the adsorption process, where the removal ability will increase with an increase in surface activity and kinetic energy of the adsorbate when the solution temperature is higher. However, high-temperature conditions can also damage the physical structure of the biosorbent so that it has the potential to reduce the removal ability of the biosorbent, especially if the temperature is too high for the biosorbent. If the adsorption ability of the biosorbent is getting better along with the increase in the temperature of the solution, then the adsorption process occurs endothermically. Namely an increase in adsorption ability caused by an increase in the mobility of the dye molecules accompanied by an increase in the active group (active site) on the adsorbent.

Conversely, if the adsorption process decreases along with the increase in the temperature of the solution, then the adsorption process occurs exothermically which causes a decreasing adsorption ability for both the dye molecule and the active site of the adsorbent due to an increase in the temperature of the solution[30)]. Fig. 9 also shows that the adsorption ability decreased along with increasing the solution's temperature. The adsorption capacity that decreases with increasing solution temperature can be caused by the adsorbent losing its properties, one of which is the surface structure that can bind pollutant molecules[33)].

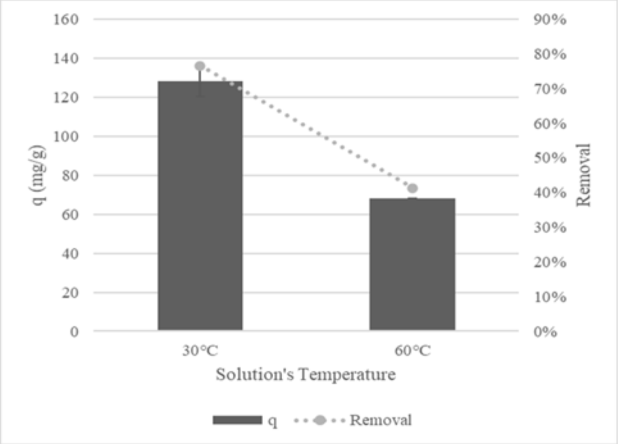

Fig. 9: Effect of Solution's Temperature

3.8 Isotherm and Kinetics

The adsorption isotherm analysis aims to determine the form of interaction between the adsorbate (pollutant) and the adsorbent. The results show that the Langmuir isotherm is the suitable model that can represent the form of interaction between the adsorbate and the adsorbent in this study. It is concluded based on the coefficient of determination (R^2) of the Langmuir isotherm which is closer to one. These results are per research conducted by Kannan et al., (2010)[19)]. In the Freundlich isotherm, the higher the value of 1/n (n>1), the higher affinity between the adsorbate and the adsorbent will increase the heterogeneity of the binding site of the adsorbent. In the results of this experiment, it can be identified that the value of 1/n is <1 so that there is a difference in energy levels at each existing binding site, which prevents the multilayer adsorption process from occurring. The large value of K_F also indicates that the adsorption process occurs exothermically, where the higher temperature of the solution, the lower number of adsorbed pollutants.

Table 1. Isotherm Value

Isotherm	Parameter	Unit	Value
Freundlich	K_F	((mg/g) (L/mg))	7.212
	1/n		0.370
	R^2		0.938
Langmuir	q_m	(mg/g)	55.556
	K_L	(L/mg)	0.110
	R^2		0.996

The adsorption kinetics analysis of an adsorption experiment was carried out to understand the process of the adsorption mechanism that occurs. In this study, three types of adsorption kinetics models were used, namely pseudo-first-order, pseudo-second-order, and intraparticle. The three types were chosen based on the consideration that they are the most representative kinetics to explain the mechanism that occurs in adsorption with biosorbents. Based on the results of experiments conducted to identify the kinetic model of the reaction that occurs, it can be concluded that the adsorption process that occurs is suitable with the pseudo-second-order adsorption kinetics model as evidenced by the coefficient of determination that is closest to one, which is 0.9945. While the coefficient of determination of pseudo-first-order is 0.9787 and intraparticle diffusion has a coefficient of determination of 0.8373. These results indicate that the adsorption process occurs by chemisorption (adsorption process that occurs with chemical reactions) which involves the exchange of electrons between pollutant molecules and functional groups on the surface of the adsorbent [22)].

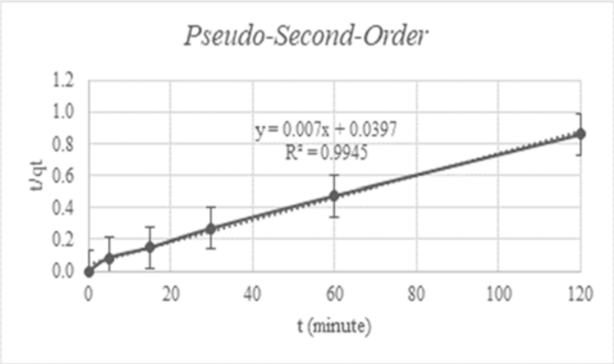

Fig. 10: Graph of Pseudo-Second-Order, the Kinetics Model that Represents the Adsorption Process in this Experiment

4. Conclusion

The potential utilization of wild algae biomass as a biosorbent of dye has been studied. The Soxhletation+H_2SO_4 activation method (DAB-S) has been shown as the best removal among tested activation methods. Parametric study showed that the highest Brilliant Green removal up to 97% can be achieved at biosorbent dosage 0.5 g/L, dye concentration 80 mg/L, pH 6, and temperature 30°C. Assessment of adsorption isotherm and kinetics indicated the adsorption mechanism followed the Langmuir model (K_L=0.11 L/mg and q_m=55.556 mg/g) and pseudo-second-order kinetics.

Acknowledgments

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Nomenclature

C_{pol}	Concentration of Pollutant (mg/L)
C_{ads}	Concentration of Biosorbent (g/L)
q	Adsorption Capacity (mg/g)
q_m	Maximum adsorption capacity (mg/g)
BOD	Biochemical Oxygen Deman
COD	Chemical Oxygen Demand

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