Research Article

Adsorption Study of Methylene Blue and Methyl Orange Using Green Shell (*Perna Viridis*)

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Abstract: Green shell is generally disposed of and become environmental contaminants. In this study, the green shell was used as material to adsorb dyes residue: methylene blue and methyl orange. Green shell waste from seafood was prepared by removing the dirt then dried at room temperature. It was followed by roughly crushing before being placed in the furnace at temperatures of 300, 500, 700 and 900 °C. The selected adsorbents were sieved at 200 mesh. The adsorbents were characterized by SEM-EDX to evaluate their elements and morphology. Furthermore, the adsorption process was evaluated by determining the kinetic adsorption models. The results of the SEM characterization showed a homogeneous surface. The optimum capacity of methylene blue adsorption occurred at an activation temperature of 500 °C shells with 1 g of adsorbent at pH 7 and at 30-minute contact time, while methyl orange adsorption occurred at an activation temperature of 900 °C with 1.5 g of adsorbent at pH 10 and at 45-minute contact time. Adsorption kinetics results obtained from the variation of time with the initial adsorbate concentration showed the kinetic model of both methylene blue and methyl orange adsorption onto the adsorbent followed a pseudo-second order.

Keywords: Green shell, adsorption, methylene blue, methyl orange

Introduction

In line with the development of the industry, industrial wastes increase both in volume and type. There are many types of industrial waste, depending on the raw materials and processes used by each industry. One of them which is the most affecting for the environment is dyes. Dyes have been widely used in several industries, such as textiles, leather, paper, printing, cosmetics and so on, which, however, lead to serious environmental problems [1][2][3]. Dyes are classified into three broad categories: (a) anionic: direct, acid, and reactive dyes; (b) cationic: all basic dyes and (c) nonionic: dispersed dyes [4]. Methylene blue is characterized as cationic dye and methyl orange is anionic one [5].

Various methods have been developed and used for the removal of dye contaminants from wastewater, including physical, chemical, and biological processes. One of the chemical processes is adsorption [6]. The adsorption methods currently appear to offer the best potential for overall treatment, and it could be expected to be promising for a wide range of compounds due to its low cost [7].

Utilization of coastal waste is one alternative to deal with dye contamination that easily being obtained and inexpensive. Seafood waste is widely used in handling dyes such as shellfish particularly green shells that contains 95% - 98% calcium carbonate ($CaCO_3$) [8]. Calcium carbonate is known as a polar compound which can support the function of a green shell as a good adsorbent. By using the calcination process, $CaCO_3$ will be composed to CaO and CO_2 then the resulting calcium oxide can be used as an adsorbent to adsorb heavy metals, organic compounds and dyes.

In this research, green mussel shells was used as a dye adsorbent for methylene blue and methyl orange which are categorized as azo dyes. Determination of adsorption capacity of the adsorbent was carried out with several adsorption variables; such as calcination temperature, adsorbent mass, pH and contact time.

Materials and Methods

Spectrophotometer UV-Vis (*Hitachi UH 5300*), Scanning Elektron Microscope (SEM) (*Phenom ProX*), Furnace (*Vulcan A-550*), Waterbath Shaker (*SCILOGEX SK-O330-Pro*). The Materials used in this research were green shell, distilled water, filter paper, methylene blue and methyl orange. All materials were acquired in pro analysis (p.a.) quality from Merck, Germany.

Preparation of the green shell adsorbent

Green muscle shells were obtained from a seafood stall waste in Yogyakarta, at first the shell was cleaned, grinded using mortars and pestle to get fine particles then calcined using a furnace at variation temperature of 300 °C, 500 °C, 700 °C, and 900 °C for 5 hours respectively. Afterwards, the calcined shells were put in a desiccator for 1 hour and sieved at 150 mesh.

Adsorption Study

Effect of temperature on the preparation of the green shell hell adsorbent

The obtained adsorbents from the various calcination temperature were weighed to 0.05 g and placed into a beaker containing 10 ml of methylene blue and methyl orange with a concentration of 25 ppm. The mixture was shaken for 15 minutes at room temperature then filtered with filter paper and analyzed with UV-Vis spectrophotometer at the maximum wavelengths.

Effect of the mass adsorbent on the adsorption process

Adsorbents with the optimum performance of adsorption from the variation calcination temperature were weighted to 0.05, 0.5, 1, and 1.5 g then placed into a glass beaker containing 10 ml of methylene blue and methyl orange dyes with a concentration of 25 ppm. The solution was shaken for 15 minutes at room temperature then filtered using filter paper and analyzed by UV-Vis spectrophotometer at maximum wavelengths.

Effect of the pH on the adsorption process

The solution of methylene blue and methyl orange with the volume of 10 mL were prepared respectively at a concentration of 25 ppm with the buffer pH of 4, 7 and 10. The selected adsorbents with the best performance from the variation of calcination temperature and mass were added into the solution then shaken for 15 minutes. Then the mixture was filtered with filter paper and analyzed using UV-Vis spectrophotometer.

Effect of the contact time on the adsorption process

The selected adsorbents were added into a beaker glass that already contained 10ml of methylene blue and methyl orange solution with a concentration of 25ppm. Each mixture was shaken with time variations of 5, 10, 20, 30, 40, 50, 60, 90 and 120 minutes at the optimum pH. The mixtures were then filtered and analyzed using a UV-Vis spectrophotometer.

Results and discussion

Material characterization

In this study, the calcination process was carried out at various temperatures of 300 °C, 500 ° C, 700 °C, and 900 °C in order to observe the effect of temperatures to the chemical composition of the adsorbents. The previous study has observed that $CaCO_3$ content in the shells converted to CaO via calcination process following the chemical reaction (1).

$$CaCO_3 \text{ (s)} \leftrightarrow CaO \text{ (s)} + CO_2 \text{ (g)} \qquad\qquad (1)$$

Calcination is a pyrolysis process at temperatures of 400 - 900 °C, in which the purpose of calcination is to remove volatile compound contained in the substance. The exothermic calcination reaction is shown in reaction (2). [8] [9][10]

$$CaO\ (s) + CO_2\ (g) \leftrightarrow CaCO_3\ (s) \qquad\qquad (2)$$
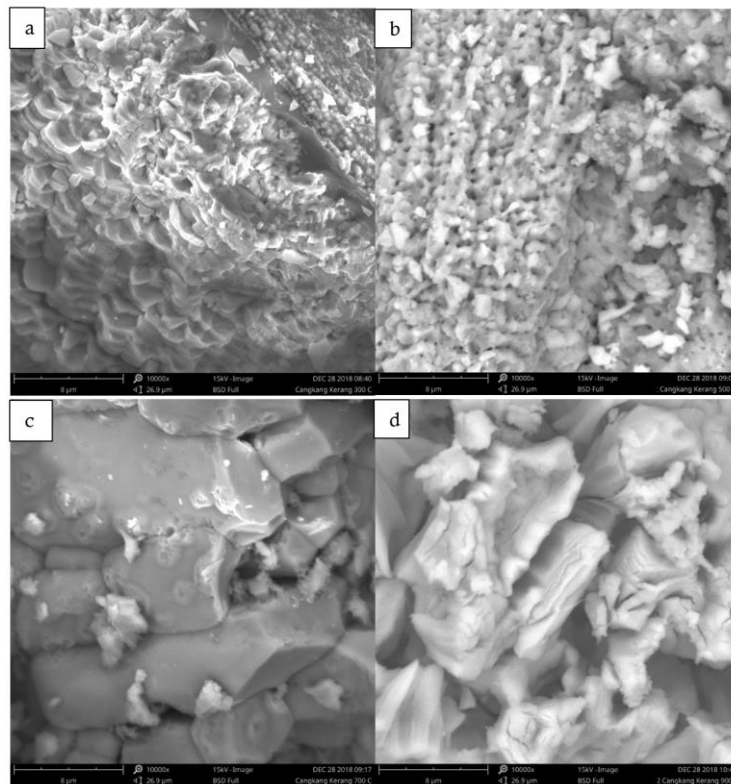
**Figure 1**. SEM images of the adsorbents that were calcined at a) 300 b) 500 c) 700 d) 900 °C

Figure 1. showed morphology of the adsorbents that formed a bulk or irregular lumps with varying sizes. The effect of temperature variation is used to find the optimum temperature from the process of the green shells adsorption process against methylene blue and methyl orange.
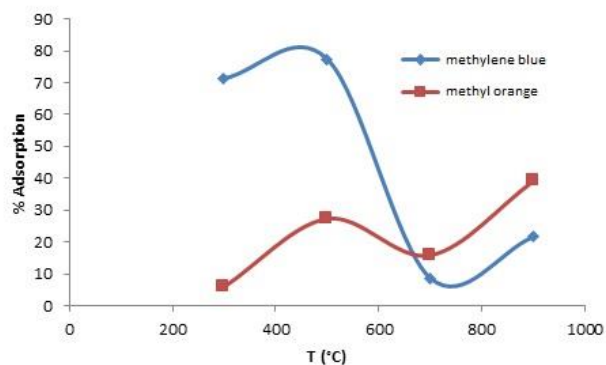
**Figure 2**. Effect of the calcination temperature on the adsorbents performance in the dyes adsorption

In Figure 2., performance of the adsorbents from various calcination temperature was determined via adsorption process. The highest adsorption of methylene blue occurred using the adsorbent calcined at a temperature of 500 °C with the % adsorption of 77.429% and the highest adsorption of methyl orange was

occurred using the adsorbent calcined at 900 °C with % adsorption value of 39.067%. The difference risen in the absorption process was affected with several factors such as the property of the adsorbent, the property of the adsorbate, the property of the solution and the contact time [11]. In the adsorption process, polarizability of adsorbate will increase the adsorption ability of molecules with high polarizability (polar) or could attract against other molecules compared to ones that cannot form a dipole (non-polar). Moreover, contact time is influenced by the amount and form of porosity of the adsorbent, adsorbents with a large porosity form have a higher absorption ability, so that the adsorption is likely to undergo faster [12].
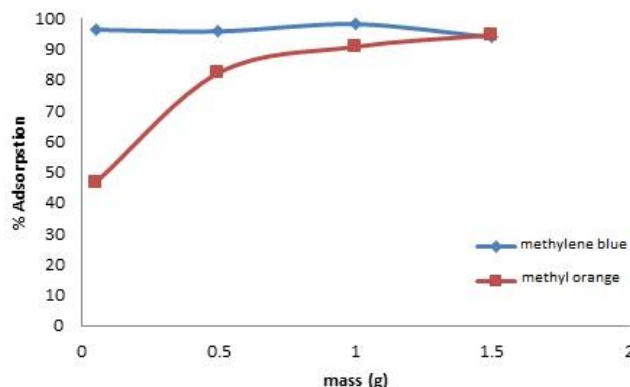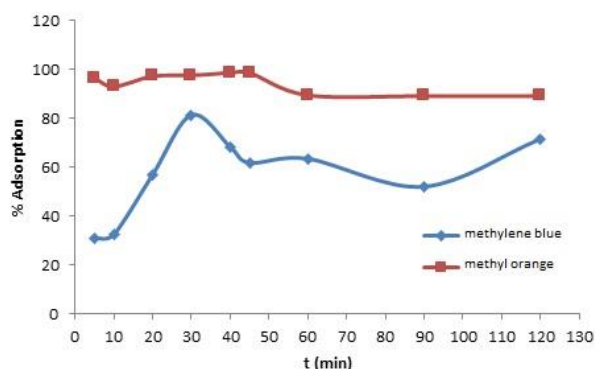

Figure 3. Determination of optimum mass

From Figure 3., it could be observed that optimum % of methylene blue absorbed by the adsorbent using the adsorbent mass of 1 g with the % adsorption capacity is 98.193%. Meanwhile, the optimum % of methyl orange absorption was occurred using the adsorbent mass of 1.5 g with % absorption i94,651%. This showed that the higher the activation temperature, the more pores were opened in the adsorbent so that the dye could be more easily absorbed into the adsorbent of the green shell.
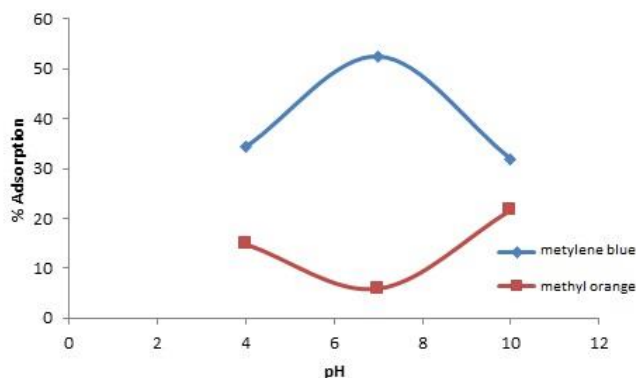
Figure 4. Determination of the optimum pH

The optimum condition was depicted in Figure 4. for the adsorption of methylene blue was underwent at pH 7 with the % adsorption of 52.5% and the one for the adsorption of methyl orange was at pH 10 with the % adsorption of 21.68%. For the methylene blue adsorption, as it is a basic dye that give positively charged ions when dissolved in water, thus, in acidic medium positively charged surface of sorbent tends to oppose the adsorption of cationic sorbate species[13]. When the pH of dye solution increase, the surface tends to acquire its negative charge, thereby resulting in an increased adsorption of dyes due to increasing electrostatic attraction between positively charged sorbate and negatively charged sorbent reached its maximum at pH 7. However, as the pH increases, the number of hydroxyl groups in the solution is higher as well, thus competed with the attraction between dye and adsorbent surface.

Furthermore, for the methyl orange adsorption, the structure of this dye is affected by pH of solution. Methyl orange is more likely to present in the state of quinone (with negative charge at -SO$_3$ and positive charge at -N(CH$_3$)$_2$ group) at acidic medium and in the state of azo (with negative charge at --SO$_3$ group) at the basic one [14]. Therefore, its adsorption at basic and acidic medium is higher due to these charges interaction with the adsorbent that has a positive charge site from calcium and negative charge site from oxygen.

Figure 5. Determination of the optimum time

In Figure 5., it could be observed that the optimum time for methylene blue adsorption was at 30 minutes with 81.43% adsorption, meanwhile for methyl orange was at 45 minutes with % absorption of 98.671%. Contact time is one of the factors that influence the adsorption process. According to the collision theory, speed of the reaction depends on the number of collisions at a time. The more collisions the faster the reaction takes place until the equilibrium conditions is achieved. The best time is the time of equilibrium between the adsorption and desorption rates [15]. To determine the interaction between adsorbent and adsorbate, the kinetics of the adsorption reaction was determined.

Table 1. Adsorption kinetics of the adsorbent against dyes

Adsorption kinetics						
Dyes	Pseudo first order			Pseudo second orded		
	$qe_{1\ (mg/g)}$	$k_{1\ (min^{-1})}$	R	$qe_{2\ (mg/g)}$	$k_{2\ (min-1)}$	R
Methylene blue	0.6534	-0.009212	0.2608	0,9124	1.7970	0.9451
Methyl orange	1.000009901	9.9029x10^{-6}	0.3347	0.15189	0.5538	0.9962

Adsorption kinetics was used to determine the rate of adsorption that is affected by time. Based on the data in Table 1., each dye adsorption process followed the reaction kinetics of pseudo second order. The pseudo second order kinetics model shows the balance of the adsorption process between adsorbate and adsorbent but does not depend on concentration and only depends on the time of adsorption.

Conclusion

Green shells are effectively used as adsorbents in the adsorption of methylene blue and methyl orange as it contains CaCO$_3$. The optimum conditions for adsorption of methylene blue was using calcination temperature adsorbents of 500 ℃ with an adsorbent mass of 1 g at pH 7 at contact time of 30 minutes. Meanwhile, for the methyl orange adsorption, the optimum condition was using adsorbent from 900 ℃

calcination temperature at contact time of 30 minutes, adsorbent mass of 1.5 g, pH 10 and contact time of 45 minutes.

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