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INFLUENCE OF HEAT TREATMENT ON EGGSHELL PARTICLES AS LOW COST ADSORBENT FOR METHYLENE BLUE REMOVAL FROM AQUEOUS SOLUTION

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ABSTRACT
The influence of heat treatment on eggshell particlesas low cost adsorbent of methylene blue had been studied. The eggshell particles were heated at variation temperatures of 150ºC, 200ºC and 300ºC. Heated eggshell particles were then used as an adsorbent for methylene blue removal from aqueous solution. The effects of contact time and pH on adsorption capacity of methylene blue were also studied. The results showed that the optimum temperature of the heat treatment was obtained at 200ºC, where the adsorption capacity was 0.197 (mg/g) and percentage of removal was 98.58%. The adsorption studies showed that optimum adsorption occurred at contact time 15 minutes and pH of 12. Adsorption of methylene blue by the heated eggshell particles fitted the Langmuir and Freundlich isotherm equations. The maximum adsorption capacity (Q_{max}) of methylene blue was 0.321 (mg/g).
Keywords: Eggshell particles, methylene blue, adsorption, heat treatment, temperature.

INTRODUCTION

Textile industry is one of growing sectors in Indonesia, even today the textile industry is a major source of foreign income to the country. The development of textile industry certainly has some advantages. Beside some advantages, it also has negative impact on the environment. Negative impact in the production of the textile industry is a liquid waste dye produced from the coloring process. During the fabric dyeing in the wet process, there are dyes that adsorbed and partly not adsorbed and then left behind in wastewater. When wastewater with high levels of these dyes are dumped into the river or into the sewer without treatment, then this causes water pollution and environmental degradation.[1]

The commonly used dye in the textile industry is benzene group such as methylene blue. Methylene blue is a thiazine dye which is often used to dye silk, wool, cosmetics, paper, and office equipment. Methylene blue is one of organic pollutants and non-biodegradable. It has benzene groups which is difficult to be degraded. Methylene blue has a dark blue color, crystal shape and also the important basic dye in the cloth, leather, and cotton fabrics dyeing process. Due to cheap price and availability, the utilization of methylene blue is increase and consequently the wastewater containing methylene blue is also increase. Methylene blue is one of toxic aromatic hydrocarbon compounds that can cause harmful effects, such as gastrointestinal irritation, and irritation of the skin. In addition, methylene blue in textile waste is also mutagenic, carcinogenic and difficult to be degradated by microorganisms.[2]

Several methods had been done to reduce pollution of dyes such as filtration, flocculation, ozonation, coagulation, adsorption, precipitation, cation exchange, photodegradation and biodegradation.[3,4] However, the most common method used for wastewater treatment is the adsorption method because the process and the equipment is simple. The adsorption process using an adsorbent is one of the easiest methods. It is low cost and also known as an effective process for reducing dyes from wastewater.[5] Several types of adsorbents have been used for adsorption process in dye wastewater treatment such as zeolite, rice husk ash, activated charcoal, bentonite and eggshell membrane.[6]

Several studies have been conducted to obtain inexpensive alternative adsorbents such as fiber, activated carbon from rice husk, hardwood, chitosan, banana, silica, bentonite, peat.[7-13] Natural manganese mineral, oil shale ash, alum sludge, zeolite, activated alumina, and natural graphite mineral manganese, oil shale

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ash, activated alumina, and graphite. Nowadays, it has been also developed adsorbent for the adsorption of methylene blue dye such as activated carbon shell of coffee inserted TiO_2 photocatalyst, and shrimp shells.[14] In addition, the eggshell is also one of adsorbent alternatives to solve the problem of dye pollution water.

Many researches had been done to take advantage of eggshells in many different applications, such as fertilizers, feed additives, heavy metal adsorption and organic compounds adsorption from wastewater.[15] The chemical composition of eggshell is 94% of calcium carbonate, 1% of magnesium carbonate, 1% of calcium phosphate and 4% of organic compounds. It has porous structure which contains 7000-17000 of pores.[16] Compared with other adsorbent, eggshell is easily found and processed into adsorbent. By using the eggshell as an effective and economical adsorbent can certainly help people to cope with both the waste bin from the eggshell itself and waste textile dye produced from the textile industrial factories.

Eggshells had been used as adsorbents for the removal of certain substances. Eggshell was utilized by Zulfikar *et al.* for the adsorption of components lignosulfonate.[17] Muhammad *et al.* used eggshell for adsorption of oil.[18] The activated eggshell had been used for the adsorption of Pb from battery waste.[19] Belay and Hayelom had made use of eggshell for methyl orange dye adsorption.[20] The utilization of eggshell particles with heated treatment for adsorption of methylene blue dye has not been reported. Therefore, in this study eggshell particles was heated and used as an adsorbent of methylene blue. The heat treatment was done with the purpose to enlarge the pores and remove impurities by breaking the bonds of chemical or oxidizing of surface molecules, resulting changes in physical properties where surface area increase in size and influence the adsorption capacity. The purpose of the heat treatment was also to expand the pore diameter and increase the amount of pore. In this work, we studied the effect of heat treatment of eggshell particles on their methylene blue adsorption capacity. The adsorption was carried out on a variety of contact time, pH, and initial concentration of methylene blue. The concentration of methylene blue was observed by using UV-Vis spectrophotometer.

EXPERIMENITAL

Material and Methods

Methylene blue (MW: 319.86, MF: $C_{16}H_{18}ClN_3S$) used in this study was of commercial purity and used without further purification. Eggshell was collected from the local restaurants in Darussalam, Banda Aceh. Indonesia.

Preparation of eggshells as an adsorbent

1 kg of eggshell was washed with water to remove impurities attached to the surface of the eggshell. Furthermore, the washed eggshell was separated between the shell and the membrane and then dried in an oven at a temperature of 105°C for 1 hour. The dried eggshell was crushed into particles and sifted with a 100 mesh sieve and then weighed as much as 500g. Furthermore eggshell particles were heated with furnace on temperature variation of 150°C, 200°C and 300°C for 1 hour.

The yield of the eggshell particles was obtained by comparing the weight of the eggshell particles before heated by the weight of eggshell particles that has been heated and the calculation was as follow:

$$\text{The yield (\%)} = b / a \times 100\% \qquad (1)$$

Where, a was weight (g) of the eggshell particles before heating and weight (g) of eggshell particles after heating (g)

Adsorption study of methylene blue by eggshell particles

The process was carried out with a variety of conditions parameters of a previous study.[6] Stock solution concentration of methylene blue was 1000 ppm which was prepared by dissolving 1 gram of methylene blue in 1000 mL of distilled water. Maximum wavelength was determined by using 1 ppm methylene blue solution. Calibration curve was obtained from various concentrations of methylene blue 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 5.0, and 7.0 ppm. The absorbance was measured by using UV-Vis spectrophotometer at maximum wavelength previously obtained was 665 nm. The results were plot in the graph with absorbance as the y-axis and concentration as the x-axis to get the form of a linear calibration curve.

In order to study the influence of heat treatment of eggshell particles on its performance for methylene blue removal from aqueous solution, 2 gram of each heated eggshell particles (150°C, 200°C and 300°C) and eggshell particles without heated treatment were added to each erlenmeyer glasses containing 20 mL of 20 ppm of methylene blue solutions. The mixtures were stirred using a shaker with a speed of 250 rpm for 20 minutes, then filtered with filter paper. Once the adsorption process was completed, the filtrate obtained from each erlenmeyer glasses were examined their methylene blue absorbance values by using UV-Vis spectrophotometer at a wavelength of 665 nm. Absorbance values obtained were then inserted into the regression equation to determine the concentration of the final methylene blue dye, and then the absorption capacity of dye and dye removal percentage were calculated by using the following formulas:

$$Q = \frac{(C_0 - C_t)\,V}{m} \quad (2)$$

$$Removal\ (\%) = \frac{C_0 - C_t}{C_0} \times 100\ \% \quad (3)$$

Where, C_0 was initial concentration of the methylene blue, C_t was final concentration of methylene blue, V was volume of solution and m was mass of adsorbent.

Influence of contact time and pH on methylene blue adsorption by heated eggshell particles were also studied in this work. In order to study influence of contact time, the contact time was varied from 5 to 25 minutes. To study the influence of pH, the pH of initial solutions were adjusted with various pH of 6, 8, 10 and 12 by using HCl and NaOH solutions. The experiments were also conducted by various initial concentrations of methylene blue (5, 10, 20, 40, and 60 ppm) in order to study the equilibrium adsorption isotherm of methylene blue by heated eggshell particles. Langmuir (Eq.-4) and Freundlich (Eq.-5) equations were used as adsorption isotherm models.

$$\frac{C}{Q} = \frac{1}{K_L Q_{max}} + \frac{C}{Q_{max}} \quad (4)$$

$$\log Q = \log K_F + \frac{1}{n}\log C \quad (5)$$

RESULTS AND DISCUSSION

Preparation and characterization of heated eggshell particles

Eggshell particles were heated by using a furnace with a temperature variation of 150°C, 200°C and 300°C. The yield of each heated eggshell particles were shown in Table-1.

Table-1: Results of heated eggshell particles

Temperature of heat treatment (^{0}C)	Weight (g)	Yield (%)
150	10	98.9
200	10	97.4
300	10	95.2

It was observed that the yield of the obtained adsorbent decreased with increased in temperature. The lowest yield was obtained at a temperature of 300°C. The heat treatment temperature of eggshell particles was inversely to the yield of obtained adsorbent. The increase in temperature causes the decrease of water content in the eggshell particles resulting the decrease of the yield. The color of eggshell particles was change by heat treatment as shown in Fig.-1.

The increase in heat treatment temperature caused the different color of obtained adsorbents. The color of eggshell particles heated at a temperature of 200^{0}C was yellowish and different with the color of eggshell particles heated at a temperature of 150^{0}C. The heat treatment at a temperature of 300^{0}C produced a brown adsorbent. It was due to the decomposition of organic compounds in the eggshell particles as described by Witoon.[21]

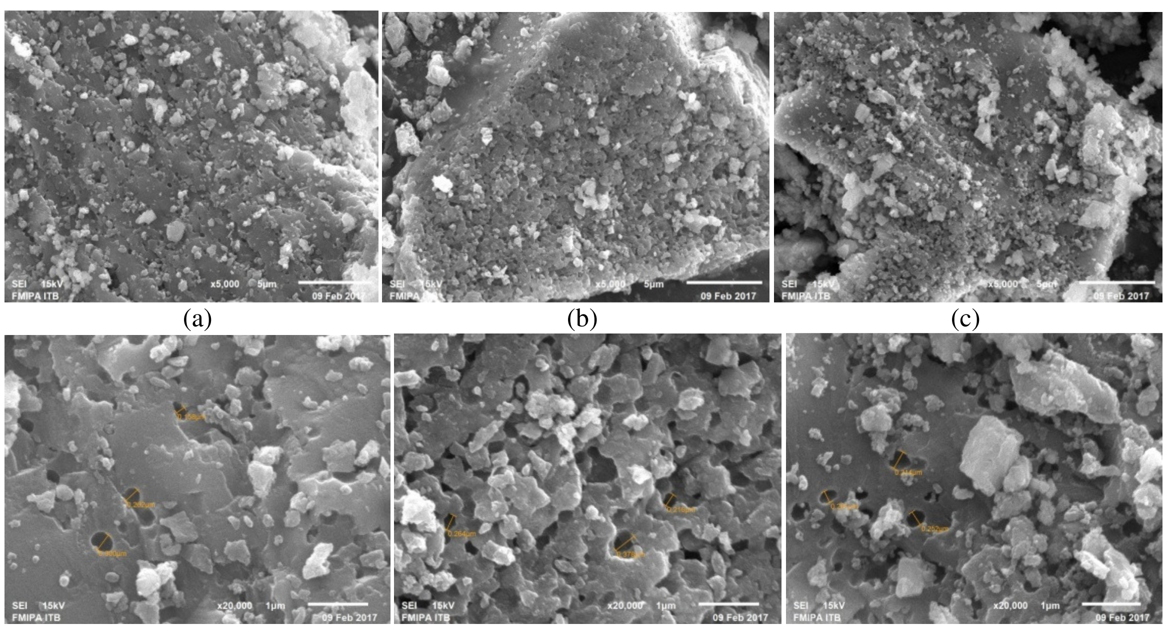
The heat treatment is a process to develop the pore structure by thermal decomposition, thus indirectly affect the size of the density of the adsorbent produced as shown by the yield results in Table-1.

Adsorption capacity of the adsorbent can be increased by the heat treatment to provide desired properties. Heat treatment of the adsorbent aimed to enlarge the pores by breaking chemical bonds or oxidize molecules on adsorbent surface and change the nature of physics that is growing larger surface area. Moreover, the purpose of this process is also to enhance the pore volume, pore diameter expands, and it may cause some new pores.

a b c d

Fig.-1: Appearance of eggshell particles (a) without heated and heated at (b) 150^{0}C (c) 200^{0}C (d) 300^{0}C

Figure-2 shows the SEM images of eggshell particles heated at 150ºC (a, d), 200ºC (b, e) and 300ºC (c, d) with diffferent magnification (500 and 20.000x). The average pores size of eggshell particles heated at 150ºC, 200ºC, and 300ºC were 0.240 0.286 and 0.256μm, respectively. The pore diameters of eggshells particles heated at 200ºC and 300ºC were larger than eggshell particles heated at 150ºC. However at heat treatment temperature of 300ºC, the eggshell particles showed many pores filled by decomposed and damaged components, moreover the pores were destroyed due to the heating.



(a) (b) (c)

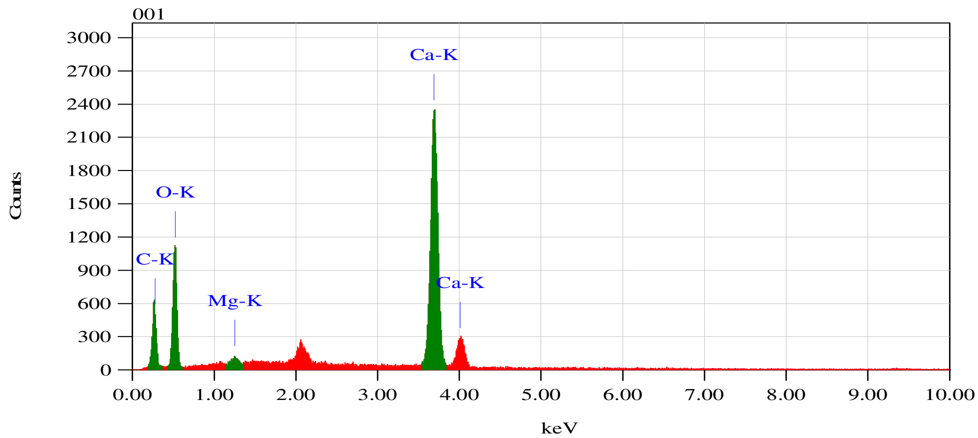
(d) (e) (f)

Fig.-2: SEM images of eggshell particles heated at 150ºC (a, d), 200ºC (b, e) and 300ºC (c, d) with diffferent magnifications (500 and 20.000x).

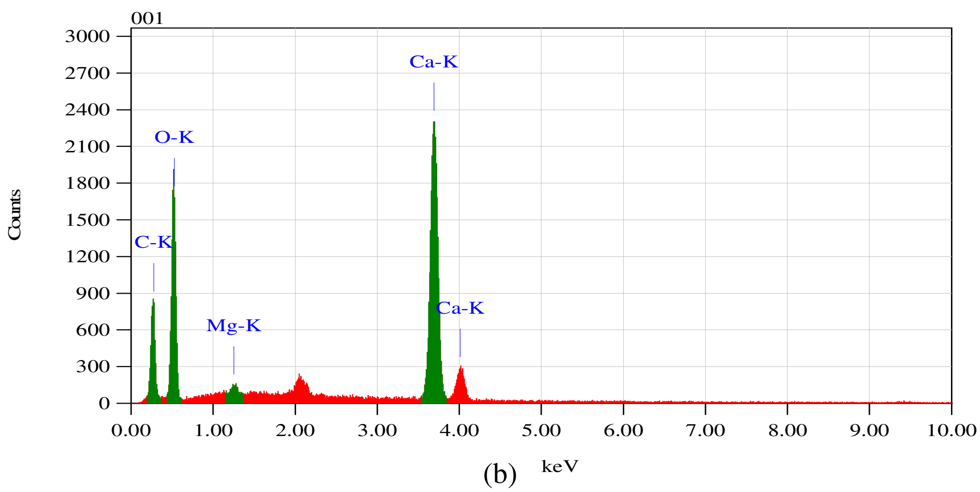
EDS data of heated eggshell particles were shown in Figure-3. Based on ZAF method standardless quantitative analysis, it was found that the mass percentages of C, O, Mg and Ca elements of eggshell particles heated at 150ºC were 22.58, 53.545, 0.38 and 23.59%, respectively.

Eggshell particles heated at 200ºC contained 20.59, 48.49, 0.39, and 30.53% of mass percentages of C, O, Mg and Ca elements, respectively. Mass percentages of C, O, Mg and Ca elements of heated eggshell particles at 300ºC were 20.87, 53.01, 0.34, and 25.78%, respectively.

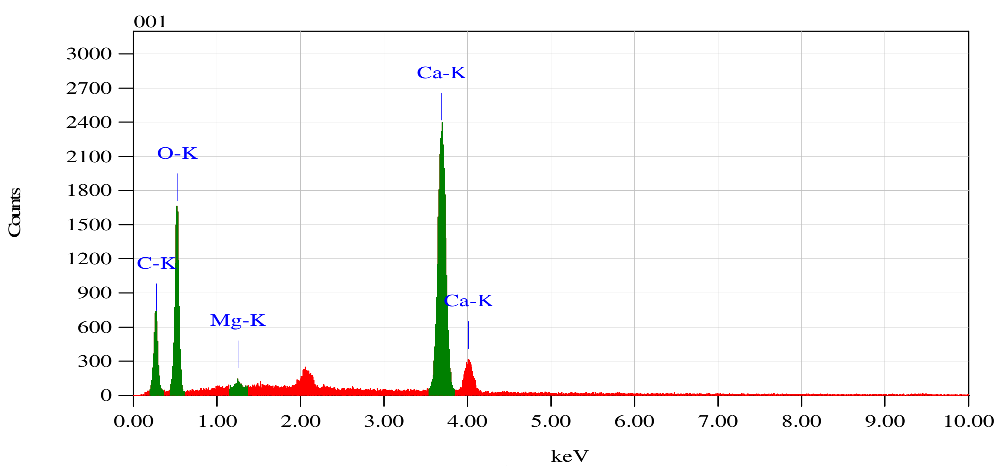
The mass percentage of Ca element of heated eggshell particles at 200ºC was higher than mass percentage of Ca element of heated eggshell particles at 150ºC and 300ºC. It was probably the reason why the highest adsorption capacity of methylene blue found when the adsorption was conducted by using heated eggshell particles at 200ºC.



(a)



(b)



(c)

Fig.-3: ED's data of eggshell particles heated at (a)150 ºC, (b)200 ºC and (c) 300ºC

It was known that the main component of adsorbent was $CaCO_3$ that served as active site for methylene blue adsorption. The different of mass percentage of each elements of eggshell particles at different heat treatment temperature was due to the decomposing of organic compounds. Witoon reported that TGA pattern of eggshell showed two distinct stages of weight losses. The weight loss of the first stage (below 680°C) was due to adsorbed water and loss of organic compounds.[21]

Adsorption study of methylene blue by eggshell particles

Initially, adsorption experiment was conducted by using eggshell particles without heat treatment, followed by eggshell particles which were already heated at a temperature of 150°C, 200°C and 300°C. The results were shown in Figure-4.

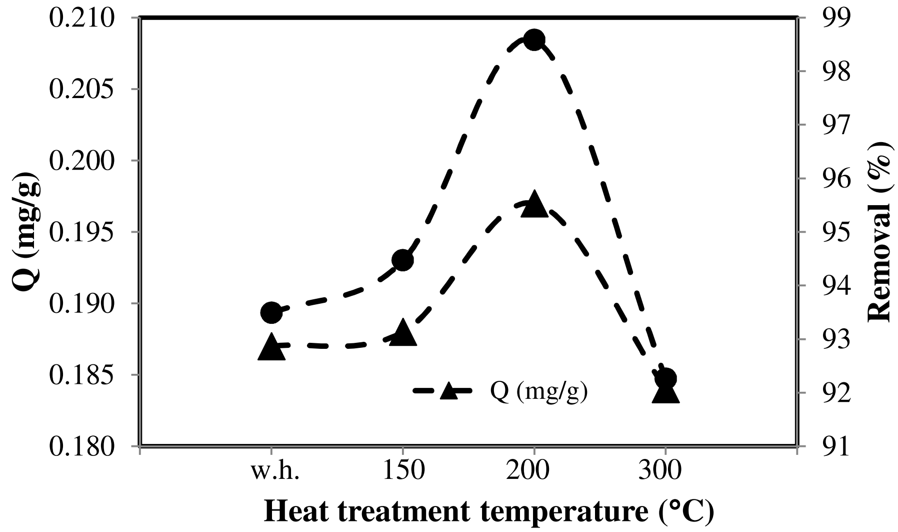


Fig.-4: Influence of heat treatment temperature on adsorption capacity and removal percentage of methylene blue.

Figure-4 shows heat treatment temperature of eggshell particles affected the adsorption capacity (Q) and removal percentage of methylene blue. Eggshell particles without heat treatment (w.h.) showed low adsorption capacity and removal percentage of methylene blue. Heated eggshell particles showed the increase methylene blue adsorption capacity and maximum at heat treatment temperature of 200°C. It indicated that heat treatment improved methylene blue adsorption capacity of eggshell particles. Based on SEM analysis, the heated eggshell particles at 200°C showed more open and larger pores than heated eggshell particles at 150°C and 300°C. Therefore, the methylene blue molecules easily came into the pores of eggshell particles and the adsorption capacity increased. Furthermore, adsorption capacity was decreased by using eggshell particles heated at 300°C. It was due to the functional groups of proteins and mucopolysaccharides contained in the eggshell paticles such as carboxyl (COOH), amine (NH_2) and sulfonate (SO_2O^-) that served as active sites of adsorbent became damaged and resulting the adsorption capacity decreased.The damage could be observed from the color of eggshell particles that turn into black ash when heated at a temperature of 300°C as shown in Figure-1. Based on this results, the eggshell particles with heat treatment temperature of 200°C that had the highest adsorption capacity was choosen as the best adsorbent for removal methylene blue and then used for further treatment.

Effect of contact time

The contact time is one of factors that influence the adsorption process. In order to study the effect of contact time on methylene blue adsorption by heated eggshell particles, the experiments were conducted with contact time 5 to 25 minutes and the adsorbent used was eggshell particles which were heated at 200°C. The obtained results are shown in Fig.-5.

The adsorption capacity of methylene blue by heated eggshell particles increased from 0,145 (mg/g) to 0.152 (mg/g) with increasing contact time from 5 to 15 minutes. It was due to at a longer contact time,more active sites of heated eggshell particles contacted with methylene blue molecules thus increasing the adsorption capacity. However, the increase of contact time to 20 minutes decreased the adsorption capacity and tended to be constant at longer time (25 minutes). It was due to the adsorption equilibrium had been reached at contact time of 15 minutes, where the active sites of heated eggshell particles had been saturated by methylene blue molecules. With increasing of contact time, some adsorbed methylene blue molecules went back to the solution due to the shaking.

In this study, the equilibrium contact time obtained was 15 minutes. This contact time was shorter than reported by Salman *et al*.[6] They reported that the equilibrium contact time was 30 minutes for adsorption of methylene blue by eggshell without heat treatment and eggshell membrane. The short equilibrium time is one of economical factors on selection of adsorbent. The equilibrium contact time obtained in this study was used for further treatment.

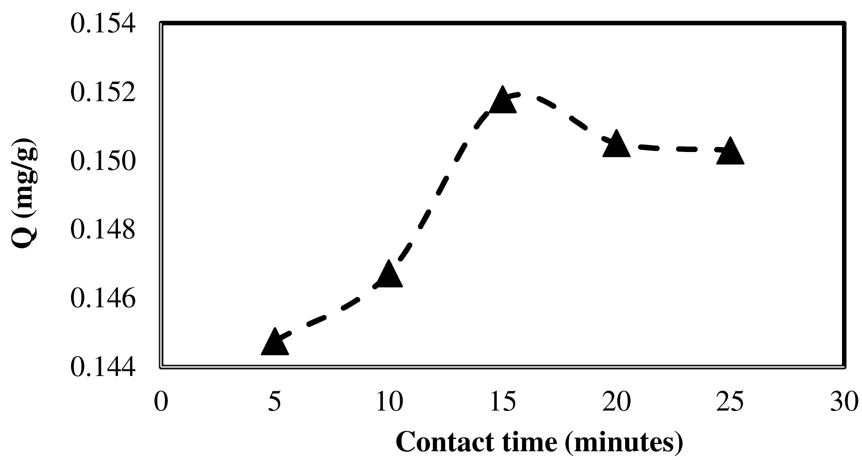


Fig.-5: Effect of contact time on the adsorption capacity of methylene blue by heated eggshell particles.

Effect of pH

Adsorption capacity of an adsorbent depends on the pH (acidity) of the dye solution, because the pH affectsthe adsorption process on the surface of the adsorbent. In order to study the effect of pH on methylene blue adsorption by heated eggshell particles, the experiments were conducted with various of pH (2-12). The pH of initial methylene blue solutions were adjusted by using HCl and NaOH solutions. The obtained results were shown in Fig.-6.

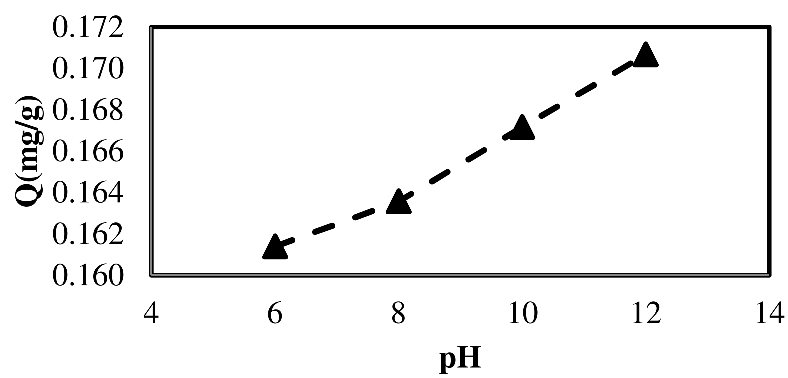


Fig.-6:The effect of pH on the adsorption capacity of methylene blue by heated eggshell particles

Figure-6 shows the increase of adsorption capacity of methylene blue by heated eggshell particles with increasing pH. It proved that the pH of the solution is one of the parameters that affects the adsorption.

Heated eggshell particles more effectively adsorbed methylene blue in alkaline. It was due to at alkaline solution the particles of heated eggshell particles contained a lot of negative charges especially carbonate species such as H_2CO_3, HCO^{3-}, and CO_3^{2-} that served as active sites of methylene blue molecules that has positive charge.The low adsorption capacity of methylene blue in acidic pH might be due to the H^+ ions existed in the solution. The H^+ ionscompeted with methylene blue to enter active sites available on the heated eggshell particles. In addition, when HCl was added, the calcium dissolved and formed calcium chloride, water and released carbon dioxide gas[21]. The same results were also reported by Norzita *et al.* and Salman *et al.* for eggshell without heat treatment and eggshell membrane.[6, 22]

Effect of initial concentration of methylene blue

Effect of initial concentration of methylene blue was studied by conducting the experiment with various methylene blue initial concentrations of 5, 10, 20, 40, and 60 ppm. The pH of solutions was adjusted to pH 12 and the adsorption process was conducted for 15 minutes at a speed of 250 rpm. The results were shown in Fig.-7.

Figure-7 shows the increase of adsorption capacityof heated eggshell particles from 0,048 (mg/g) to 0.32 (mg/g) with increasing initial concentration of methylene blue from 5 to 40 ppm. However, at an initial concentration of 60 ppm, the adsorption capacity tended to be constant. Panthania *et al*. stated that the higher the initial concentration of the solution, the more the amount of solute that can be adsorbed untill the equilibrium reached.[23]

The ability of adsorbent on adsorption has a limitation. The maximum concentration capable adsorbed by the heated eggshell can be determined by using the adsorption isotherm equations. There are two common adsorption isotherm equations used in the adsorption process namely Langmuir and Freundlich adsorption isotherm equations (Eq.-4 and 5). The results of calculation were shown in Table-2.

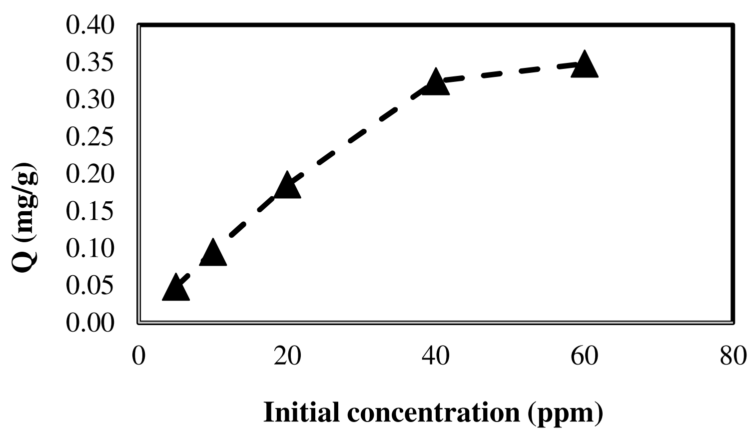


Fig.-7: The effect of initial concentration on adsorption capacity of menthylene blue.

Table-2: The Langmuir and Freundlich adsorption isotherms of methylene blue by heated eggshell particles

Langmuir isotherm			Freundlich isotherm		
Q_{max} (mg/g)	K_L	R^2	K_F (mg/g)	n	R^2
0.321	1.009	0.98	8.334	2.447	0.92

The correlation coefficient (R^2) of Langmuir and Freundlich adsorption isotherms where 0.98 and 0.92, respectively. It indicated that the adsorption of methylene blue by heated eggshell fitted to both Langmuir and Freundlich adsorption isotherm equations where the values of R^2 were more than 0.9. Langmuir isotherm assumes that the adsorbent covered by monolayer of adsorbate and homogeneous. Freundlich isotherm equation assumes that the adsorbent covered by more than one surface layer (multilayer) and the heterogeneous.The maximum adsorption capacity of methylene blue by heated eggshell particles obtained in this work was 0.321 mg/g.

CONCLUSION

The optimum heat treatment of eggshell particles obtained at a temperature of 200ºC with adsorption capacity of 0.197 mg/g and removal percentage of 98.58%. The optimum condition of methylene blue adsorption by heated eggshell particles obtained at pH 12 for 15 minutes. The adsorption of methylene blue by heated eggshell particles fitted Langmuir and Freundlich adsorption isoterms where the maximum adsorption capacity was 0.321 mg/g.

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