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Using quail eggshell to treat methylene blue in aqueous solution

Sử dụng vỏ trứng cút xử lý xanh methylen trong môi trường nước

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Abstract

In this study, the raw quail eggshell powder (RQEP) was utilized as a cheap and environmentally friendly adsorbent to remove methylene blue (MB) from aqueous media under different conditions. The morphology of the prepared adsorbent was determined by scanning electron microscopy. The Langmuir and Freundlich isotherm models were used to model the adsorption data. The obtained results showed that the adsorption of MB on RQEP was well-fitted with the Freundlich model. The optimal conditions for the MB adsorption were also established. The RQEP material has been shown to be effective in MB treatment in aqueous solution with a maximum adsorption capacity of 11.47mg/g.

Keywords: Eggshell; adsorption; methylene blue.

Tóm tắt

Trong nghiên cứu này, bột vỏ trứng cút thô (RQEP) được sử dụng như là chất hấp phụ giá rẻ và thân thiện với môi trường để loại bỏ xanh methylen (MB) trong môi trường nước ở nhiều điều kiện khác nhau. Hình thái của vật liệu được xác định bằng phương pháp kính hiển vi điện tử quét (SEM). Mô hình đẳng nhiệt Langmuir và Freundlich được dùng để kiểm tra tính phù hợp của quá trình hấp phụ MB trên vật liệu RQEP. Kết quả cho thấy quá trình hấp phụ MB trên vật liệu RQEP phù hợp với mô hình Freundlich. Điều kiện tối ưu cho quá trình hấp phụ này đã được khảo sát và thiết lập. Kết quả nghiên cứu cho thấy vật liệu RQEP có hiệu suất cao trong xử lý MB với dung lượng hấp phụ tối đa là 11.47mg/g.

Từ khóa: Vỏ trứng; hấp phụ; xanh methylene.

1. Introduction

Nowadays, water is becoming scarcer due to the overexploitation of freshwater resources by humans as well as the pollution of wastewater discharged from industries. Various contaminants present in wastewater include dyes, heavy metals, solids, organic and inorganic chemicals, directly and indirectly threaten the habitat of all living things. Among these pollutants, synthetic dyes are hazardous compounds widely found in effluents of textile, dyeing, printing, food plant and dyestuff

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manufacturing [1]. Annually, an amazingly large amount of color wastewater is directly discharged into the environment [2]. It is noticed that it causes many damages to the environment and living things organisms due to its deep color, high solubility and low degradation rate [3]. Just low concentration (less than 1 ppm) in aqueous solution, MB may reduce the light penetration, photosynthesis, impact of the aesthetic beauty of water resources and even cause skin irritation, and dysfunction of reproductive or central nervous system [1]. So, it is essential to treat MB before releasing into the water cycle.

Thus, many methods have been reported for treating MB in aqueous solution such as chemical oxidation [4], photocatalysis [5], coagulation [6], hyperfiltration [7], biological treatment [8] and adsorption [9]. Among them, adsorption is commonly used owing to its low cost, high efficiency, large selectivity and regeneration ability [9]. A variety of adsorbents is available for the MB removal, including fly ash [10], activated carbon [1], coffee [12], chitosan [13], sawdust [14], rice husk [15], red mud, pinus bark [16], orange peel [17], bagasse [18], and durian peel [19].

In particular, the use of eggshell is pertinent because it is an abundant waste produced by the food industry, economical and eco-friendly due to its availability and absence of any toxic and hazardous constituent's elements, and as efficient as the more expensive activated carbon. Eggshell represents 9%–12% of the total egg weight, consisting of 94% calcium carbonate ($CaCO_3$), 1% calcium phosphate ($Ca_3(PO_4)_2$), 1% magnesium carbonate ($MgCO_3$), and 4% water and other organic matters [20]. Quail eggs are popular and widely consumed in Vietnam. Therefore, there is a large amount of quail egg shells being discharged daily. Discarded quail eggshells are only used for the purpose of making fertilizers, or livestock additives; most of quail eggshells will be discharged into the environment, causing pollution. Therefore, taking advantage of this raw material to treat wastewater has both environmental and economic value. Previous studies have indicated the high efficiency of eggshells for removing metals (e. g., Cu(II), Zn(II) [20], Cr(VI) [21]) and dyes (e.g., remazol brilliant violet-5R [22], methyl red [23]).

In this study, the raw quail eggshell powder (RQEP) were used as an adsorbent in the removal of MB from aqueous solution and was characterized to evaluate its morphological and chemical properties. The effects of various parameters, including pH, contact time, initial concentration, adsorbent dose, and temperature on the MB adsorption were investigated to determine the optimal conditions for MB adsorption process.

2. Materials and methods

2.1. Materials and chemicals

All reagents used were of analytical grade and were obtained from Sigma Aldrich Chemical Company, including methylene blue ($C_{16}H_{18}C_lN_3S$, 98%), hydrochloric acid (HCl, 36.5%), and sodium hydroxide (NaOH, ≥98%). The pH of the aqueous solutions was adjusted with 0.01M NaOH or HCl. The aqueous solutions were prepared using distilled water.

The quail eggshell waste was collected from Thanh Khe Market, Danang, Vietnam. The eggshells were washed many times with distilled water and dried in an oven at 80^oC. Then the dried quail eggshells were crushed and ground in the grinder to convert to a fine powder of 0.15mm particles. The collected RQEP was stored in a sealed bottle (Fig.1) and ready to use in the study.

Fig. 1. RQEP material preparation for MB adsorption

2.2. Adsorption experiments

Adsorption experiments were carried out by using bath procedure at room temperature. The stock solution of MB (1000mg/L) was prepared by dissolving 1g MB in 1000mL distilled water. For each adsorption experiment, a mixture of a defined amount of RQEP and 25mL of MB solution of defined concentration were agitated in the flask at a constant speed of 150rpm and the determined time period. After the stirring time, the liquid phase was separated from the residue by a centrifuge at speed of 5000rpm/min for 15min. After the adsorption reached equilibrium, the adsorbent was centrifuged and the residual concentration of MB was measured using a UV-VIS Spectrophotometer. The influence of the solution pH (3 - 13), contact time (3-240min), dye concentrations (5-60mg/L), adsorbent dose (5-120g/L), and temperature (25 – 55^{o}C) on the MB adsorption were evaluated.

The percentage of dye removal (R, %) and amount of adsorbed dye (q, mg/g) by RQEP were calculated by Eqs (1) and (2), respectively:

$$R = \frac{C_O - C_e}{C_O} . 100 \quad (1)$$

$$q = \frac{(C_O - C_e)V}{m} \quad (2)$$

where C_o and C_e are the initial and equilibrium concentration of MB (mg/L), m is the mass of RQEP (g), and V is the volume of solution (L)

2.3. Analytical method

The concentration of the MB solution was measured by a UV-VIS spectrophotometer (T80+, PG Instrument) at a wavelength of 665 nm. The morphology of RQEP particles was observed using Scanning Electron Microscopy (SEM, JOEL 5410 – LV).

3. Results and discussion

3.1. Surface characterization

The morphology of RQEP described in the SEM image (Fig. 2 a, b) shows that the prepared adsorbent presents a rough surface with tiny pores. The magnified image of RQEP (Fig. 2b) demonstrates the presence of irregular structure with heterogeneous particle sizes in the range of 0.01 - 0.1µm.

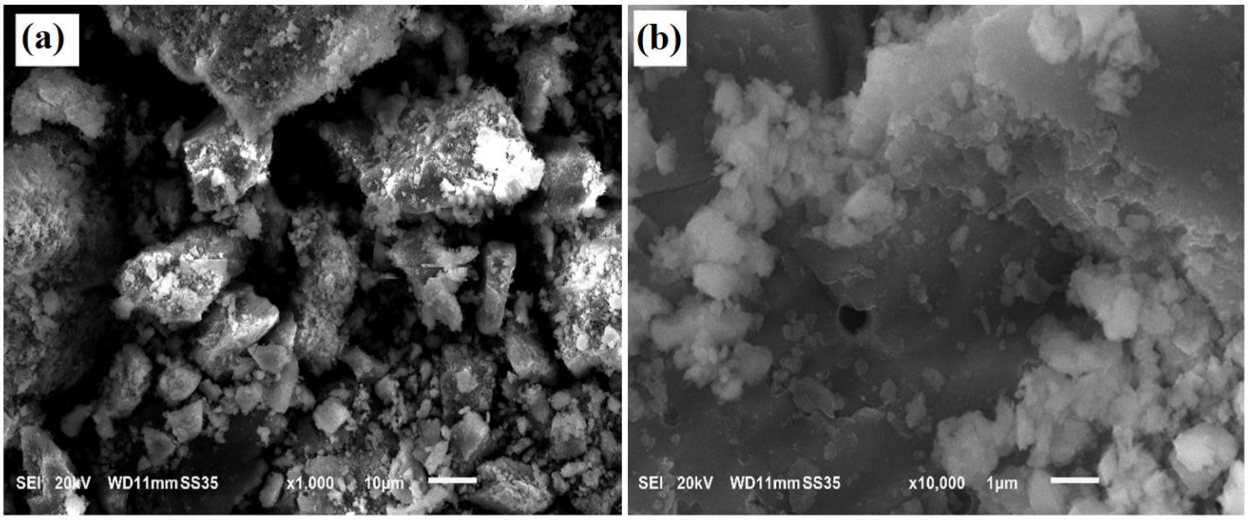

Fig.2. SEM image for RQEP material
(a) Ratio x1000, (b) Ratio x10000

3.2. Effect of pH

The solution pH plays a significant role in controlling MB adsorption onto RQEP. As shown in Fig. 3a, the percentage removal of MB by RQEP raised as the pH increased. Specifically, between pH 3-7, the MB adsorption efficiency increased slowly from 61.20% to 73.85%. While increasing the pH from 7 to 9, the MB adsorption capacity increased sharply from 73.85% to 91.62%. After that, the adsorption performance of RQEP hardly changed much. Therefore, in the following experiments, pH 9 was chosen as the optimal pH. This observation can be explained by the fact that at low pH, the adsorbent surface is positively charged so competitive adsorption between H^+ and MB ions takes place to bind to hydroxyl and carboxyl groups. With increasing pH, the surface of the material becomes negatively charged due to the increase of OH^- ions; facilitating the MB adsorption due to the enhancement of electrostatic attraction [25].

3.3. Effect of contact time

Contact time is an important parameter because it reflects the adsorption kinetics of adsorbent for a given solution concentration of adsorbate. According to the obtained result, shown in Fig. 3b, the adsorption efficiency of RQEP was dramatically enhanced with an increasing stirring time. Particularly, the adsorption of MB on RQEP rapidly occurred in the first 3min, reaching an efficiency of 81.85%. After that, the uptake efficiency of MB gradually rose with increasing a contact time. Continuing to increase time to the end of the survey, the MB removal capacity of RQEP was almost unchanged, remaining at 91.62%.

It can be seen that the MB adsorption process of RQEP occurred in two stages: the first stage was when the solute particles diffuse rapidly to the surface of the adsorbent, the second stage was when the adsorption rate increased slowly until reaching equilibrium because the adsorbent sites were occupied mostly by the adsorbate molecules [26]. The higher the adsorption time, the higher the interaction and contact between MB in water and the material, so the efficiency increases with increasing adsorption time. From the above research results, the optimal time was chosen to be 90min.

3.4. Effect of adsorbent dose

The survey results of the adsorbent dose effect displayed that the MB adsorption efficiency increased as rising adsorbent dose. As shown in Fig. 3c, the amount of RQEP increased from 0.1 to 1.5g, the performance increased sharply from 86.60 to 92.23%. Then, further increasing with the dosage from 60g/L up to 80g/L, the adsorption capacity increased from 92% to 96% and then showed a tendency to saturate. This can be explained that at the same pollutant concentration, when the content of the adsorbent increases, the adsorption efficiency increases. However, the efficiency reaches its maximum value and remains constant because the adsorption centers become redundant for the adsorbent [26].

3.5. Effect of temperature

The effect of temperature on the removal of MB by RQEP was investigated and shown in Fig. 3d. From the results, it was observed that the percentage removal of MB by RQEP steadily declined from temperatures 25 to 55°C (drop from 91.64% to 83.76%). The percentage of removal of MB decreased to 63.50% when the temperature was increased to 55°C. Generally, the higher the temperature, the lower the adsorption efficiency. This result can help us to predict that the adsorption process is exothermic and the adsorption mechanism is mainly physical [28]. These results seem to indicate that a high temperature works against the removal of MB. Therefore, a temperature of 25°C is selected as the optimum temperature for adsorption.

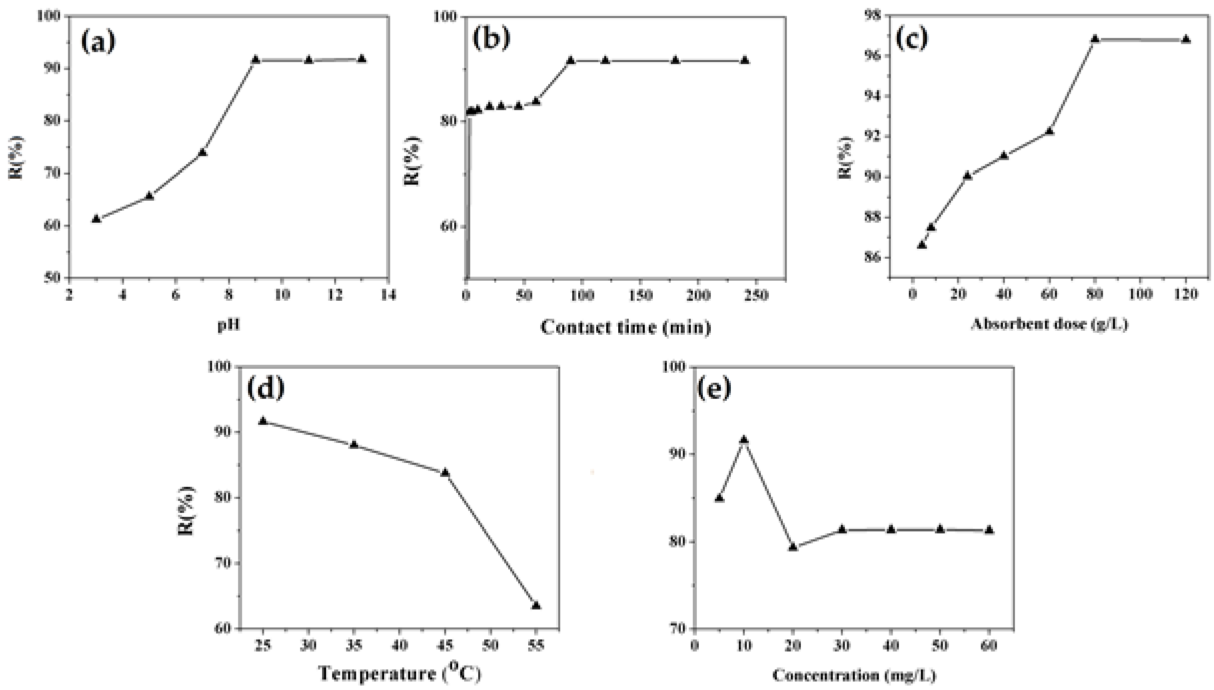

Fig 3. Evolution of the MB removal versus **a**. pH, **b**.contact time, **c**. RQEP dose, **d.** temperature, **e**. initial concentration, , (pH = 9, contact time = 90min, initial concentration C_o= 10mg/L, adsorbent dose = 8g/L, temperature = 25◦C)

3.6. Effect of initial concentration

As depicted in Fig. 3e, when the concentration increased, the adsorption efficiency of RQEP for MB also increased. At the concentration of 5 - 10mg/L, the removal efficiency increased slightly from 84.93% to 91.62%; continued to increase the concentration from 10mg/L to 20mg/L, the adsorption efficiency tended to decrease sharply from 91.62 - 79.36% and then barely changed at 81% until the end of the survey. With a certain amount of adsorbent, the decreasing adsorption efficiency when increasing the concentration of adsorbent can be confirmed that the adsorption center is saturated and cannot be adsorbed any more [24].

3.7. Adsorption isotherm model

The Langmuir and Freundlich isotherm models are two popular models used to describe the adsorption process. In particular, the Langmuir isotherm equation describes the adsorption process on a homogeneous adsorption surface and is widely used to process adsorption data as well as calculate the maximum adsorption capacity in the real adsorption processes. Meanwhile, the Freundlich model is an empirical equation that applies to adsorption on heterogeneous surfaces. The Langmuir and Freundlich isotherm adsorption models can be represented by Eqs. (3) and (4), respectively:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{Q_{max} K_L} \quad (3)$$

$$Lnq_e = LnK_F + \frac{1}{n} LnC_e \quad (4)$$

where Q_{max} is the maximum amount of MB per unit mass of adsorbent (mg/g); K_L is the Langmuir adsorption constant (L/mg); C_e is the concentration of MB at the time of equilibrium (mg/L); q_e is the adsorption capacity at equilibrium time of the adsorbent (mg/g); K_F is the Freundlich constant (mg/g); n is the heterogeneity coefficient. The constant K_F and coefficient n characterize the adsorption capacity and adsorption strength. The K_F and n values can be calculated according to the dependence diagram between Lnq_e and LnC_e by linear regression from experimental data.

The resulting isotherm parameters are reported in Fig. 4 and Table 1. The results in Table 1 show that the correlation coefficient of the adsorption isotherm according to the Freundlich model is found to be R^2 = 0.9919, which is higher than that of the Langmuir model of R^2 = 0.7143. Thus, the MB adsorption on RQEP is better described by the Freundlich adsorption model. This reveals that the MB adsorption on RQEP is a heterogeneous process. The constant K_F calculated according to the Freundlich model for the RQEP is 0.48.

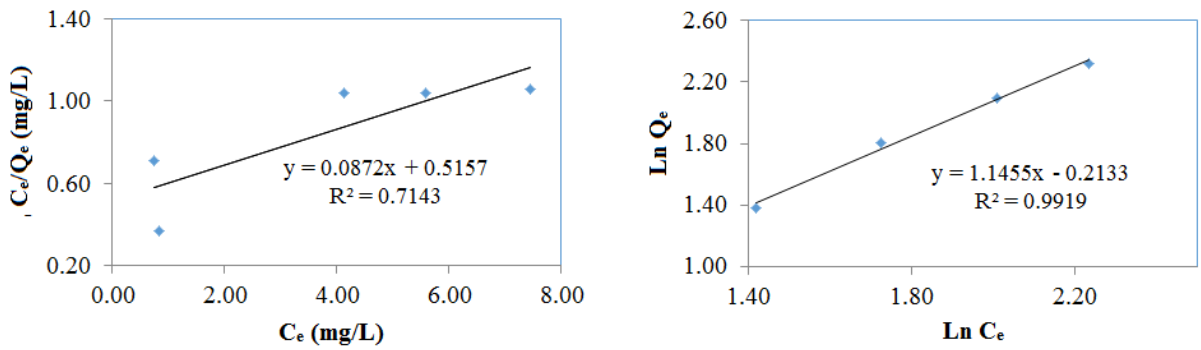

Fig. 4. Adsorption isotherm model (Langmuir and Freundlich)

Table 1. Isotherm parameters of mb adsorption on rqep materials

Langmuir				**Freundlich**		
Q_{max} (mg/g)	K_L (L/mg)	R_L (L/mg)	R^2	1/n	K_F [mg/g).(L/mg)1/n]	R^2
11.47	0.17	0.77-0.22	0.7143	1.1455	0.48	0.9919

3. Conclusion

The RQEP adsorbent was used to treat MB successfully. The adsorption capacity of this material obtained according to the Langmuir model is 11.47mg/g. The effects of pH, time, adsorbent dosage, temperature and adsorbent concentration were investigated in detail and systematically. The results showed that the adsorption capacity increased with pH, time, and dose of materials, but this ability decreased with increasing concentration and temperature. The adsorption of MB on RQEP followed the Freundlich model. This study also demonstrated that RQEP is a potential material that can be used to treat wastewater containing dyes.

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