MODIFICATION OF SUGARCANE BAGASSE AS AN EFFICIENT BIOSORBENT FOR REMOVAL OF METHYLENE BLUE IN AQUEOUS SOLUTION

SỬ DỤNG BÃ MÍA NHƯ MỘT CHẤT HẤP THỤ SINH HỌC HIỆU QUẢ ĐỂ LOẠI BỎ METYLEN XANH TRONG DUNG DỊCH NƯỚC

Nguyen Thi Thuy[1,*], Nguyen Duong Cong Thanh[2], Do Viet Hung[2], Mai Tung Duong[2], Vu Thi Mai Phuong[1]

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ABSTRACT

Pollution of the aqueous environment is increasing rapidly, thus, finding effective solutions to solve this problem is very important. Among the cheap and available adsorbent materials, sugarcane bassage and its modified forms have confirmed in its effectiveness in the removal of dyes in aqueous medium. In this study, sugarcane bassage was modified with hydrochloric acid (HCl), sodium dodecyl sulfate (SDS) and ethylenediaminetetraacetic acid (EDTA) before using for methylene blue adsorption in an aqueous solution. The obtained results show that the removal percentage of methylene blue by using sugarcane bassage modified with HCl/SDS/EDTA could achieve the value higher than 95% when using. The modified sugarcane bassage can be applied for adsorption of methylene blue or other dyes in aqueous medium on a large scale.

Keywords: *Sugarcane bassage, organic surface modification, methylene blue adsorption.*

TÓM TẮT

Ô nhiễm môi trường thủy sản gia tăng nhanh chóng, do đó, việc tìm ra các giải pháp hiệu quả để giải quyết vấn đề này là rất quan trọng. Trong số các vật liệu hấp phụ rẻ tiền và sẵn có, bã mía được biến tính và không biến tính đã được chứng minh về hiệu quả loại bỏ thuốc nhuộm trong môi trường nước. Trong nghiên cứu này, bã mía được biến tính bằng axit clohydric (HCl), natri dodecyl sulfat (SDS) và axit ethylenediaminetetraacetic (EDTA) trước khi sử dụng để hấp phụ xanh metylen trong dung dịch nước. Kết quả thu được cho thấy tỷ lệ loại bỏ xanh metylen khi sử dụng bã mía biến tính với HCl/SDS/EDTA có thể đạt giá trị cao hơn 95%. Bã mía biến tính có thể được áp dụng để hấp phụ xanh metylen hoặc các thuốc nhuộm khác trong môi trường nước trên quy mô lớn.

Từ khóa: *Bã mía, biến tính hữu cơ bề mặt, hấp phụ xanh metylen.*

[1]Hai Phong University, Vietnam
[2]Vinschool Imperia Highschool, Haiphong, Vietnam
[*]Email: v.thuynt208@vinschool.edu.vn
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1. INTRODUCTION

Entering the 21st century, the process of industrialization and modernization is being promoted, contributing to improving the quality of human life. However, that process also entails the burden of environmental pollution which water pollution cannot be ignored. The water sources in Viet Nam have been polluted seriously by discharging thousands of tons per year of synthetic dyes during the development process of textile and paper industries. This not only seriously affects production activities but also directly harms people's health.

Accompanying the development of the textile industry is the environmental pollution problems caused by dyes, especially, the synthetic dyes. They are a kind of organic compound with a complex aromatic molecular structure that is difficult to break down and decompose. It is estimated that the dyes lost ca. 10 - 15% of the weight in dyeing process, mainly due to the lost in the washing processes. These dyes have been discharged into the aquatic environment. The existence of the dye molecules can be harmful to receiving water sources. Moreover, they are not only toxic to aquatic organisms but also resistant to natural biological degradation. They are also reasons for many serious diseases in humans [1].

It is necessary to solve the water pollution, especially the water sources located in the place where we are living. There are many ways used to treat water pollution, in which the adsorption method has shown many advantages such as high adsorption effectiveness, simple process, and not requiring model devices. Recently, there have been many studies focusing on development of efficient, low cost, and eco-friendly adsorbent materials, for instance, banana pith, neem sawdust, soybean hull, sunflower seed hull, agricultural byproducts, etc. for the purification of wastewater [2]. These adsorbent materials have been used to remove harmful substances (such as lead, copper, mercury,...) in the aquatic environment. They have low cost and availability. Moreover, they are very environmentally friendly, do not add harmful agents to the environment as well as non-toxic to humans and organisms.

Sugarcane bagasse (abbreviated as SB) is a by-product of the sugarcane industry. It is one of the largest agricultural wastes in the world. It has been used as a low-cost green adsorbent for dye removal in textile effluent. The SB has a fibril structure with the main composition of 50% cellulose, 25% lignin, 25% hemicellulose, which are favorable for adsorption of organic molecules [2, 3]. To improve the adsorption capacity of SB, it can be modified by NaOH, $NaOH/H_2O_2$, HCl, H_2SO_4, and formaldehyde [2-8]. The adsorption capacity of modified SB has been confirmed for the removal of Rhodamine B [6], novacron orange P-2R [4], malachite green dye [2], basic red 46 [3], glyphosate [5], and methylene blue [7,8] in an aqueous medium.

In this study, SB has been chosen for study the of methylene blue in an aqueous medium because of its availability. Instead of being reuesused,the SB is often discharged directly into the enviromet... causing the pollution because it attracts flies and is a suitable environment for bacterial growth. Moreover, it also causes odor pollution. Therefore, the utilization of SB as a cost-effective adsorbent could provide a two-fold advantage with respect to environmental pollution. Firstly, the volume of by-products could be partly reduced, and secondly the low-cost adsorbent could reduce the pollution of wastewaters at a reasonable cost.

Sugarcane bagasse is being evaluated as a potential adsorbent the of environmental pollution. The procedure for processing SB is relatively simple, easy to implement, and can be applied on a large scale. The use of raw or modified SB to adsorb dyes in the aqueous solution is very feasible. Interestingly, the SB can be recovered, the waste is centralized for treatment, limiting emissions into the environment.

There are some studies that reported using ethylenediaminetetraacetic acid (EDTA) to denature adsorbents such as oyster shells, fly ash, etc. for improvement of the adsorption ability of these materials in the removal of heavy metal ions from aqueous solutions [9, 10]. However, the study on using HCl/SDS/EDTA to denature sugarcane bagasse has been limited in the report. Therefore, in this study, we have tried a combination of HCl, SDS, and EDTA to modify sugarcane bagasse with the desire to prepare a highly efficient adsorbent for the removal of dyes in aqueous solutions. Moreover, the adsorption isotherms and adsorption kinetics for the methylene blue removal process by denatured sugarcane bagasse have been also studied.

2. MATERIALS AND METHODS

2.1. Materials and chemicals

Sugarcane bagasse was collected in Hong Bang, Hai Phong in September, 2022. Sodium dodecyl sulfate (SDS, 99%), Methylene blue (MB, dye content higher 82%), HCl (37%) were provided by Xilong, China. Ethylenediaminetetraacetic acid (EDTA, 99%) was purchased from Merck Co. (Germany).

2.2. Treatment of sugarcane bagasse

Step 1: pretreating with water and drying

First, preparing and measuring the weight of raw SB. Next, washing SB with clean water to remove dirt and drying SB to a constant mass. Weighing SB after drying.

Step 2: washing with distilled water, drying and grinding

First, immersing SB in boiling water for 50 min to remove the residue sugars. Next, drying SB at 80°C for 26 h until to a constant mass to obtain pretreated SB. After that, grinding the pretreated SB to powdered form by using a hammer mill, ball mill1 to 100 micromet.

Step 3: modifying with HCl/SDS/EDTA

Firstly, SB powder was modified with SDS and 5% HCl solution as follows: Dissolving 3.5g of SDS into 350mL of 5% HCl solution. Adding 35g of SB powder into the above solution and stirring continuously using a magnetic stirrer at 50°C for 3h. Filtering and washing SB powder with distilled water, then drying the powder in an oven at 80°C to a constant mass to obtain SDS/HCl treated SB powder.

Secondly, SDS/HCl treated SB powder was modified with EDTA: Dissolving 1.75g of EDTA into 200mL of distilled water. Adding SDS/HCl treated SB powder into the EDTA solution, then stirring the mixture on a magnetic stirrer at 50°C for 3h. Filtering and washing SB powder with distilled water, then drying at 80°C to a constant mass to obtain denatured SB sample.

2.3. Study on the methylene blue (MB) adsorption

2.3.1. Determination of the calibration equation of MB in aqueous medium

First, a stock solution of MB with the concentration of 1000mg/L was prepared. Next, diluting the MB mother solution to 1, 5, 10, 15, 20 and 30mg/L. These solutions were measured optical density values using a UV-Vis spectrophotometer (CINTRA 40, GBC, USA) at the absorption wavelength of 663nm (this is the maximum absorption wavelength of MB solution).

2.3.2. Study on removal of MB in aqueous medium

The experiments to compare the MB adsorption ability of denatured SB sample and pretreated SB powder were performed fixed conditions: the initial concentration of MB was 10mg/L; the volume of MB solution was 50mL; the initial mass of adsorbent was 0.5g; the pH of solution was 7; the adsorption time was 3h; the adsorption temperature was room temperature (ca. 303K).

The adsorption process was carried out as follows: Firstly, 50mL of MB solution was poured into six numbered Erlenmeyer flasks. Next, the pretreated SB powder was added to flasks no. 1, 2, 3 while the denatured SB sample was added to flasks no. 4, 5, 6. Six flasks were sharked continuously in an incubation shaker (KS 3000 ic control, 20024165, IKA, Germany) for 2h. Then, the solution in each flask was filtered using filter paper before measuring UV-Vis spectrum at the absorption wavelength of 663nm. The concentration of MB in the aqueous medium at equilibrium time was calculated based on the optical density value of the solution obtained from the UV-Vis spectrum. The removal percentage of MB (H) by samples was determined according to following equation:

$$H = (C_0 - C_e)x100/C_e \quad (1)$$

Where, C_0 and C_e are the concentrations of MB in the aqueous solution at the initial and equilibrium time, respectively.

To evaluate the effect of adsorption conditions on MB removal percentage of denatured SB sample, the experiments were carried out with various parameters as follows:

+The initial concentrations of MB were 1, 5, 10, 15, 20, and 20mg/L

+The volume of MB solution was 50mL

+The initial masses of denatured SB sample were 0.05, 0.1, and 0,2g

+The pH values of solution were 4, 6, 7, 8, 10, 12

+The adsorption times were 30, 60, 90, 120, 150, 180, 240 min

+The adsorption temperature was room temperature (ca. 303K).

The reusability was also evaluated for the lifetime of denatured SB sample. The experiment was carried out with the initial concentration of MB of 1mg/L, the adsorption time of 3h, the adsorbent mass of 0.1g, pH adsorption of 7. After each time, the adsorbent was washed with distilled water and centrifuged to collect the solid part to continue for next time MB adsorption.

3. RESULTS AND DISCUSSION

3.1. The efficiency of denaturation processing

Table 1. Weight of SB samples and efficiency of denaturation processing

No.	Sample	Quantity
1	The mass of pretreated SB powder	35g
2	The mass of denatured SB sample	26g
3	The efficiency of denaturation processing	74.28%

The mass of denatured SB sample obtained after denaturation processing was 26g, indicating reached 74.28%. The decrease in mass of SB powder after denaturation processing is due to some compositions in SB such as hemicelluloses, acid-soluble lignins, protein, wax,... were separated acidic condition . Simultaneously, filtering and cleaning processes during the experiment also cause the loss in mass of SB. The efficiency of denaturation processing could be improved if we carry the experiment at a larger scale.

3.2. MB adsorption ability of modified SB samples

3.2.1. Standard curve of methylene blue in water

From the data in Figure 1, the calibration equation of MB in water has been determined as y = 0.2527x + 0.002, where x is the concentration of MB in water and y is the optical density. The linear regression coefficient (R-square) of the equation is 0.9997 that is close to 1. So, this calibration equation can be used to determine the concentration of MB in water when studying MB adsorption.

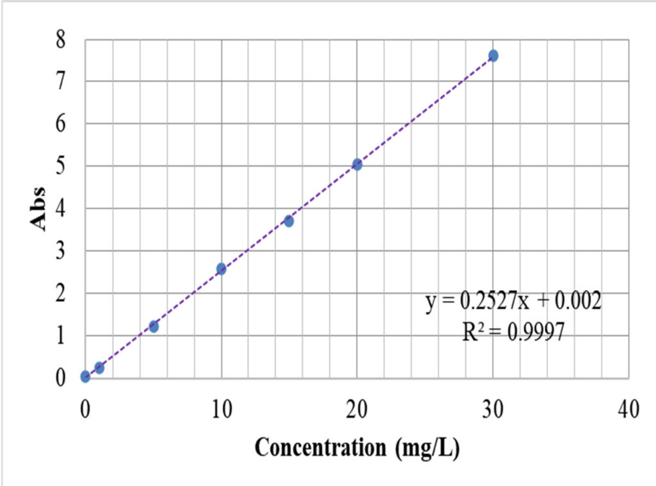


Figure 1. Standard curve of MB in aqueous solution

3.2.2. The comparison of MB adsorption ability between denatured SB sample and pretreated SB powder

Table 2. MB adsorption efficiency of denatured and pretreated SB samples

No.	Sample	MB removal percentage (%)
1	Pretreated SB powder	62.19
2	Denatured SB sample	81.50

The result from Table 2 demonstrates that denatured SB sample had a removal percentage 1.31 times higher than pretreated SB powder. This reveals the denatured SB sample is potential for removal of MB and cationic dyes in the aqueous solution. The modification with HCl/SDS/EDTA could contribute to the change in structure, morphology and composition of SB due to the reaction of hemicelluloses, acid-soluble lignins,... in SB with HCl acid as well as the attachment of SDS and EDTA onto the surface of SB fibers. The mechanism of adsorption of MB by modified SB may be the electrostatic interactions between the dyes and the surface of adsorbent [11]. These help to enhance the MB adsorption ability of denatured SB sample. The denatured SB sample will be chosen for further studies.

3.2.3. The effect of technology parameters on MB adsorption process using denatured SB sample

Table 3 presents the outcome of the MB removal percentage of denatured SB sample when using 0.05g, 0.10g and 0.20g of adsorbent in different adsorption times. It is seen that the MB adsorption efficiency increases when expanding adsorption time. For example, after 30 min of testing, the denatured SB sample only adsorbs 88.21% of MB in water while after 180 min of testing, this sample adsorbs 95.40% of MB. This may be explained that prolonging adsorption time increases exposing time between adsorbent and dye, boosting the adsorption. Notwithstanding that, extending adsorption time not only causes a minor efficiency boost, but also consumes more energy. Hence, 180 min is the suitable period for denatured SB sample to adsorb MB in water.

Table 3. The MB removal percentage of denatured SB sample when using different mass of adsorbent

No.	Adsorption time (min)	MB removal percentage (%) when using 0.05g of adsorbent	MB removal percentage (%) when using 0.1g of adsorbent	MB removal percentage (%) when using 0.2g of adsorbent
1	30	88.21	92.85	93.91
2	60	90.80	93.99	95.20
3	90	92.10	95.20	96.15
4	120	92.73	95.91	96.58
5	150	93.47	96.25	97.13
6	180	95.40	98.35	98.62
7	240	95.48	98.55	99.02

As can be seen from Table 3, denatured SB sample possesses an excellent MB adsorption ability, with the efficiency being over 88%. This is on account of porous structure, along with EDTA and SDS molecules on the surface of denatured SB sample being able to interact with methylene blue, leading to MB molecules being easily held back in the structure of denatured SB sample. The SB powder treated with HCl/SDS/EDTA showed similar MB adsorption ability to other treated SB samples which were studied by other authors. For example, the SB sample treated with NaOH could adsorb 98% of MB after 90 min of contacting [7]. The SB sample treated with running water combined with milled could adsorb 97.60% of MB in the aqueous medium at the concentration of 2mg/L and adsorbed amount 4.38mg/L [8]. As compared to adsorption ability of treated SB samples to adsorb malachite green dye [2], basic red 46 [3], Rhodamin B [6], the denatured SB sample in this work exhibited a higher adsorption efficiency.

Comparing the data of experiments with different adsorbent contents in Table 3, it could be seen that increasing the mass of denatured SB sample led to better MB adsorption efficiency. However, when increasing the mass of the adsorbent from 0.05g to 0.10g, the adsorption efficiency of the denatured SB sample had more fluctuation compared to that of sample when increasing the mass of adsorbent from 0.10g to 0.20g. Therefore, 0.1g is the optimal mass of denatured SB sample to adsorb MB in water.

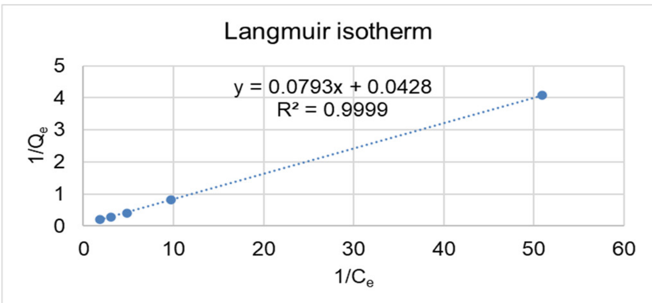
The data in Table 4 indicated that the adsorption pH influenced on the MB adsorption process by denatured SB sample. In the acidic or alkaline environment, the denatured SB sample adsorbed MB less than that in the neutral environment. This could be because of zero charge point of the denatured SB sample. The surface charge of adsorbent can affect significantly on the adsorption of cations or anions in the aqueous solution. In this study, the neutral pH of 7 is suitable for the MB adsorption process by denatured SB sample.

The results in Table 4 also show that the MB removal percentage of denatured SB sample changes negligibly when varying the initial MB concentration.

Table 4. The MB removal percentage of denatured SB sample at different adsorption pH and initial MB concentration

No.	Adsorption pH	MB removal percentage (%) when using 0.1g of adsorbent	Initial MB concentration (mg/L)	MB removal percentage (%) when using 0.1g of adsorbent
1	4	97.25	1	98.03
2	6	96.78	5	97.94
3	7	98.03	10	97.91
4	8	96.34	15	97.79
5	10	96.03	20	97.21
6	12	95.13		

3.2.4. Adsorption isotherms



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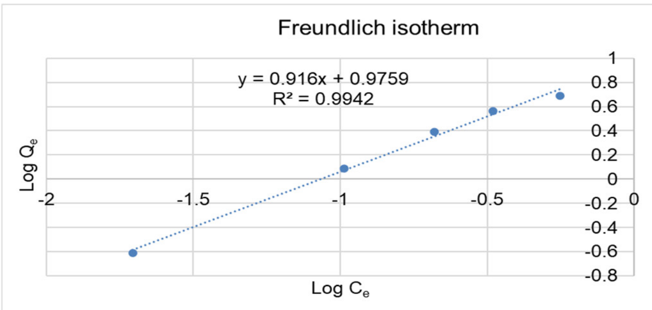

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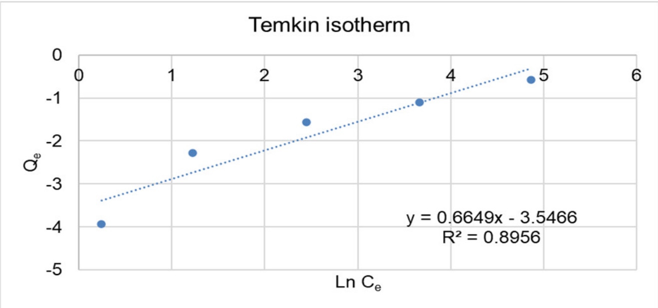

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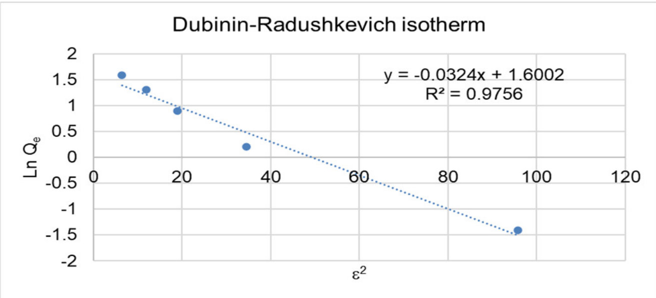


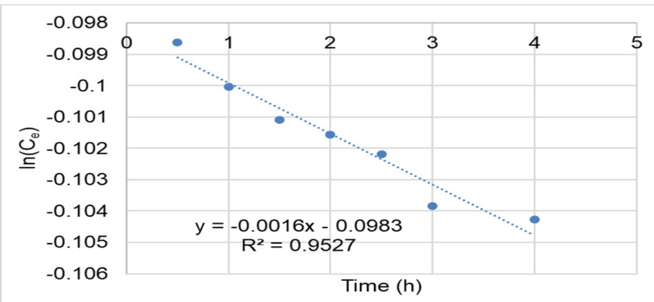
(d)

Figure 2. Isotherms with the linear equation and correlation coefficient for MB removal of denatured SB sample; (a) Langmuir isotherm, (b) Freundlich isotherm, (c) Temkin isotherm, and (d) Dubinin-Radushkevich isotherm

In this study, adsorption isotherm models used for fitting the MB adsorption data by SB sample are Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherms [9-13]. The fitting data were shown in Figure 2. These results illustrated that the adsorption process of MB by denatured SB sample was more favorable to Langmuir isotherm with R^2 = 0.9999 as the highest value when compared to other correlations in three different models. This suggests that the formation of monolayer MB on the surface of denatured SB sample was predominant [14].

3.2.5. Adsorption kinetics

Different linear kinetic models of MB adsorption by denatured SB sample including to first-order, pseudo-first-order, second-order, pseudo-second-order adsorption according to their equations and correlation coefficient values have been presented in Figure 3 [10, 15,16]. Based on the correlation coefficient values, the MB adsorption kinetic by denatured SB sample was followed by pseudo-second-order rate law. This suggests that there is a strong affinity between the denatured SB sample and the MB molecules [17].



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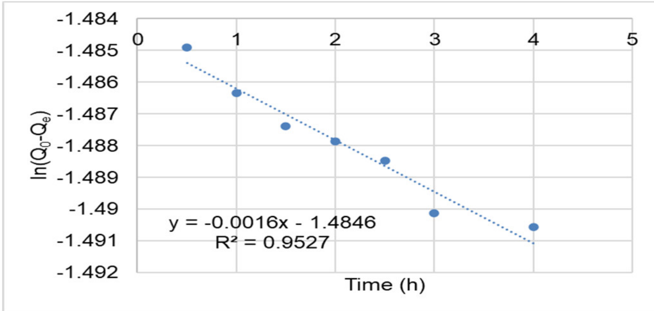

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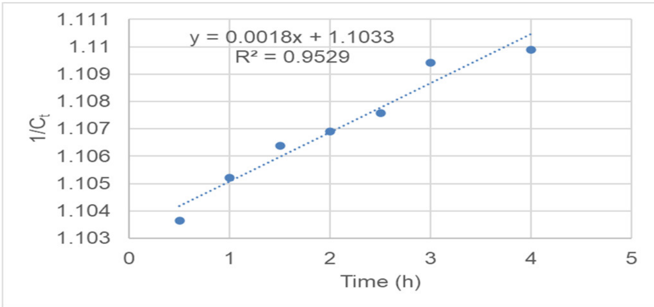

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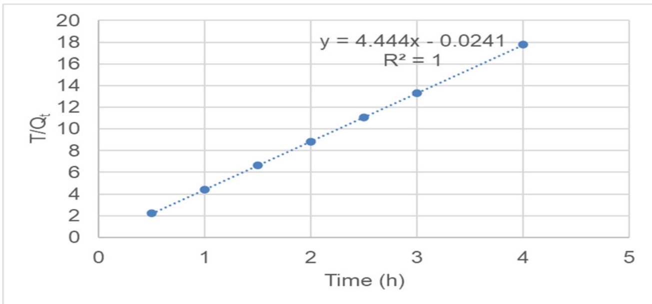

(d)

Figure 3. Reactions with the linear equation and correlation coefficient for MB removal of denatured SB sample; (a) First-order, (b) Pseudo-first-order, (c) Second-order, and (d) Pseudo-second-order

3.2.6. Reusability of denatured SB sample to adsorb MB in the aqueous solution

One of the key which determinants of what happens to the effects of a product on the environment throughout its lifetime is reusability. Because they may be reused, reusable products outperform disposable ones (which make up the bulk) in terms of life cycle impacts. The results in Table 5 indicate that the reusability of denatured SB adsorbent for adsorption MB in the aqueous solution was good. After the 4th time of use, the MB removal percentage of the sample decreases slightly.

Table 5. The MB removal percentage of denatured SB sample when reused multiple times

Number of uses	MB removal percentage (%)
1	98.35
2	97.68
3	97.17
4	96.78

4. CONCLUSION

In this study, the sugarcane bassage has been pretreated with distilled water and then treated with HCl/SDS/EDTA and applied as a bio-sorbent material for removal of methylene blue in the aqueous medium. After being pretreated and denatured, the denatured SB sample could adsorb MB in the aqueous medium much better than pretreated SB powder. The suitable conditions for the MB adsorption process using the denatured SB sample are the mass of adsorbent of 0.1g, pH adsorption of 7, adsorption time of 180 min. At these conditions, the denatured SB sample can adsorb 98.35% of MB in the aqueous solution. The MB adsorption by denatured SB sample was followed by Langmuir isotherm and pseudo-second-order rate law. The denatured SB sample could be reused to 4 times with a slight decrease in MB adsorption efficiency. The SB powder treated with HCl/SDS/EDTA is a promising adsorbent for treatment of dyes in the aqueous solution.

REFERENCES

[1]. *Water Pollution: Everything You Need to Know*. https://www.nrdc.org/stories /water-pollution-everything-you-need-know (Assess April, 14, 2023).

[2]. Hajira Tahir, Muhammad Sultan, Nasir Akhtar, Uzma Hameed, Tahreem Abid, 2016. *Application of natural and modified sugar cane bagasse for the removal of dye from aqueous solution*. Journal of Saudi Chemical Society, 20 (1), pp. S115-S121.

[3]. Juan Carlos Cueva-Orjuela, Angelina Hormaza-Anaguano, Andrés Merino-Restrepo, 2017. *Sugarcane bagasse and its potential use for the textile effluent treatment*, DYNA, 84 (203), pp. 291-297.

[4]. Saima Noreen, Haq Nawaz Bhatti, 2014. *Fitting of equilibrium and kinetic data for the removal of Novacron Orange P-2R by sugarcane bagasse*. Journal of Industrial and Engineering Chemistry, 20 (4), pp. 1684-1692

[5]. Williene Faria da Penha Bezerra, et al., 2022. *Chemical treatment of sugarcane bagasse and its influence on glyphosate adsorption*. Matéria (Rio J.) 27 (1), 1342.

[6]. Dang Van Long, 2018. *Study on adsorption of Rhodamine B dye by adsorbent from processed bagasse NaOH and NaOH/H_2O_2*. Master's Thesis in Organic Chemistry, University of Danang, (In Vietnamese).

[7]. Kamal Al-Mokhalelati, Iman Al-Bakri, Nesrin Al Shibeh Al Wattar, 2021. *Adsorption of methylene blue onto sugarcane bagasse-based adsorbent materials*. Journal of Physical Organic Chemistry, 34 (7), e4193.

[8]. Thaisa Caroline Andrade Siqueira, et al., 2020. *Sugarcane Bagasse as an Efficient Biosorbent for Methylene Blue Removal: Kinetics, Isotherms and Thermodynamics*. Int J Environ Res Public Health 17 (2), 526.

[9]. Thuy Chinh Nguyen, Trang Do Mai Tran, Van Bay Dao, Quoc-Trung Vu, Trinh Duy Nguyen, Hoang Thai, 2020. *Using modified fly ash for removal of heavy metal ions from aqueous solution*. Journal of Chemistry 2020, 8428473

[10]. Thuy Chinh Nguyen, Xuan Thai Nguyen, Do Mai Trang Tran, Quoc Trung Vu, Van Hai Nguyen, Duy Trinh Nguyen, Minh Thanh Do, Thi Len Nguyen, Thi Ngoc Lien Ly, Hoang Thai, 2020. *Adsorption ability for toxic chromium (VI) ions in aqueous of some modified oyster shell types*. Bioinorganic Chemistry and Applications, 2435777.

[11]. Denga Ramutshatsha-Makhwedzha, Avhafunani Mavhungu, Mapula Lucey Moropeng, Richard Mbaya, 2022. *Activated carbon derived from waste orange and lemon peels for the adsorption of methyl orange and methylene blue dyes from wastewater*. Heliyon, 8 (8), e09930.

[12]. Wang H., Yang L., Qin Y., Chen Z., Wang T., Sun W., Wang C., 2023. *Highly effective removal of methylene blue from wastewater by modified hydroxyl groups materials: Adsorption performance and mechanisms.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 656, 2023, 130290.

[13]. Rosly N. Z., Ishak S., Abdullah A. H., Kamarudin M. A., Ashari S. E., Alang Ahmad S. A., 2022. *Fabrication and optimization calix[8]arene-PbS nanoadsorbents for the adsorption of methylene blue: Isotherms, kinetics and thermodynamics studies*. Journal of Saudi Chemical Society, 26(1), 101402.

[14]. Rani S., Chaudhary S., 2022. *Adsorption of methylene blue and crystal violet dye from wastewater using Citrus limetta peel as an adsorbent*. Materials Today: Proceedings, 60, 336–344.

[15]. Bello M. O., Abdus-Salam N., Adekola F. A., Pal U., 2021. *Isotherm and kinetic studies of adsorption of methylene blue using activated carbon from ackee apple pods*. Chemical Data Collections, 31, 100607.

[16]. Ramutshatsha-Makhwedzha D., Mavhungu A., Moropeng M. L., Mbaya R., 2022. *Activated carbon derived from waste orange and lemon peels for the adsorption of methyl orange and methylene blue dyes from wastewater*. Heliyon, 8(8), e09930.

[17]. Wu K.H., Huang W.C., Hung W.C., Tsai C.W., 2021. *Modified expanded graphite/Fe_3O_4 composite as an adsorbent of methylene blue: Adsorption kinetics and isotherms*. Materials Science and Engineering: B, 266, 115068.

THÔNG TIN TÁC GIẢ

Nguyễn Thị Thủy[1], Nguyễn Dương Công Thành[2], Đỗ Việt Hưng[2], Mai Tùng Dương[2], Vũ Thị Mai Phương[1]

[1]Trường Đại học Hải Phòng

[2]Trường Trung học Vinschool Imperia, Hải Phòng