Vietnam Journal of Catalysis and Adsorption
Tạp chí xúc tác và hấp phụ Việt Nam

https://jca.edu.vn

# Enhancing methyl violet adsorption on sugarcane bagasse-based biochar via modification with sodium dodecyl sulfate

Nguyen Thi Thanh Nhan[1], Nguyen Thi Thu Trang[1], Le Vu Tien[1], Dao Sy Duc[1], Pham Tuan Anh[2], Dang Viet Quang[2,*]

[1] *Faculty of Chemistry, University of Science, Vietnam National University, Hanoi, Vietnam*
[2] *Faculty of Biotechnology, Chemistry and Environmental Engineering, Phenikaa University, Hanoi 12116, Vietnam*
** Email: quang.dangviet@phenikaa-uni.edu.vn*

ARTICLE INFO

Received: 04/04/2024
Accepted: 24/06/2024
Published: 30/12/2024

*Keywords:*
Biochar; Adsorption; Sugarcane bagasse; Methyl violet

ABSTRACT

In this study, sugarcane bagasse was pyrolyzed at 600 $^{o}$C in $N_2$ to generate biochar following by modification with sodium dodecyl sulfate (SDS) solution. The adsorption ability of both biochar and SDS modified biochar was examined with methyl violet. Adsorption experiments were conducted with dye solution having a different concentration at the adsorbent dose of 5 g/L. Obtained results indicated that the removal efficiency of biochar increased from 64.30% to 97.54% as the concentration of SDS modifying solution increased from 0 to 0.4 g/L, respectively. The adsorption on biochar and modified biochar fits well to Langmuir model. The maximum adsorption capacity of biochar without modification was 10.58 mg/g, but increased 14.68 mg/g after being modifying with SDS solution 0.3 g/L. The adsorption fitted well to pseudo second order kinetic model with rate constants of 0.077 and 0.161 (g/mg·min) The success of study demonstrated that the dye adsorption on sugarcane bagasse-based biochar can be significantly improved by treatment biochar with SDS solution. This suggests a facile and cost-effective way to modify biochar for dye adsorption.

## Introduction

Biochar is one of the most popular adsorbents used for the removal of contaminants from water. This adsorbent is usually produced from agricultural waste such as sugarcane, corn straw, coconut shell, sawdust, rice husk, etc. by thermal pyrolysis in an inert atmosphere [1-3]. The surface of biochar contains various functional groups that can adsorb different contaminants. Agriculture-based biochar has been investigated to remove heavy metal ions [4], dyes [5], antibiotics [6], *etc*. in water.

Sugarcane is an important crop which provides raw material for sugar, ethanol, and jaggery production industry. According to Foreign Agricultural Service/USDA, annual global sugar production reached 181.2 million tons in 2022 [7]. It is estimated that about 280 kg of wet bagasse is generated for every ton of sugar [8]. Even though, bagasse has been used as animal feed and raw material for some other industries, a huge amount of bagasse from sugar production industry is not utilized. This is a valuable and inexpensive resource for biochar production. Several works have been carried out to convert sugarcane bagasse into

https://doi.org/10.62239/jca.2024.069

biochar for contaminant adsorption [9, 10], however, raw biochar usually has low adsorption capacity [11]. Thus, significant effort has been spent to modify raw biochar to enhance its adsorption capacity. Inyang et al. found that biochar prepared by thermal pyrolysis in inert gas has Pb adsorption capacity of 31.3 mmol/kg but it increased to 653.9 mmol/kg as it was prepared in an anaerobically digested condition [11]. To enhance sulfamethoxazole adsorption on sugarcane bagasse derived biochar, Prasannamedha et al. conducted biochar activation with NaOH and as result its adsorption capacity reached 400 mg/g, higher than commercial activated carbon [12]. In another study, biochar was prepared by in-situ acid treated method to improve the toluene adsorption capacity up to 771.1 mg/g, which is three times higher than commercial activated carbon [13]. These modification methods can improve the adsorption capacity of biochar; however, they are usually complicated methods and may involve more toxic chemicals. The utilization of toxic chemicals during processing may downgrade the green nature of biochar, therefore, it requires a more benign method to modify and improve the adsorption capacity of biochar. Accordingly, the objective of this study is to find a facile and more benign method to modify sugarcane bagasse derived biochar to enhance its dye adsorption capacity. Recent studies showed that the introduction of surfactant on the surface of biochar can enhance its adsorption toward heavy metals and organic components in water [14-16]. Surfactant has been used to modify different agriculture waste derived biochar [17, 18], but, it has never been tested on sugarcane bagasse derived biochar. Thus, the purpose of this work is to modify sugarcane bagasse derived biochar with sodium dodecyl sulfate (SDS) and investigate its potential for the enhancement of methyl violet adsorption.

## Experimental

### *Materials*

Sugarcane bagasse was collected from a sugarcane juice shop in Hanoi and dried in oven at 105 °C for 24h before being cut into small pieces with size of approximately 2.0x0.5cm for later experiments. HCl (36%), and NaOH (98%) were received Xilong Scientific Co. Ltd. Metyl violet (MV) were purchased from HiMedia Laboratories Private Limited. $N_2$ gas (99.99%) and ethanol (95%) were supplied by a local supplier.

### *Biochar preparation and modification*

Sugarcane bagasse samples were pyrolyzed in tubular furnace having a diameter of 2.54 cm under $N_2$ atmosphere at 600 °C. Temperature was increased from room temperature to 600 °C at ramping rate of 10 °C/min and then maintained at 600 °C for 90 min. Biochar (BC) obtained was stored in vial for later tests and modification.

BC samples were modified with SDS by a wet method. In a typical experiment, 1 gram of BC was dispersed in SDS solution having concentration of from 0.1 to 0.4 g/L following by shaking on a shaker for 6 h at room temperature. Finally, samples were filtered, dried for 12h at 100 °C, and stored in vials for later characterization and tests. Samples were denoted as BC-SDS01, BC-SDS02, BC-SDS03, and BC-SDS04 for BC treated with SDS solution having the concentration of 0.1, 0.2, 0.3, and 0.4 g/L, respectively.

### *Characterization*

The morphology of biochar was studied by scanning electron microscopy (SEM) using JEOL 7500F coupled with Energy-dispersive X-ray spectroscopy (EDX). MV concentrations were analyzed by UV-Vis absorption method using Jenway 6850 at wavelength of 584 nm.

### *Adsorption experiment*

In a typical adsorption experiment, a desired amount of BC from 0.05 to 0.2 g was weighed and dispersed into 25 ml beaker containing 10 mL of dye solution with a desired concentration from 20 to 150 mg/L and mounted on shaker at a shaking rate of 50 rpm at room temperature (26 °C). The pH of solutions can be adjusted by the dropwise addition of NaOH 0.1 M and HCl 0.1 M. Water samples were periodically taken and analyzed for dye concentration by UV-Vis spectrophotometric method. The amount of dye adsorbed on samples; q (mg/g) was calculated according to equation (1).

$$q = \frac{(C_0 - C_e).V}{m} \quad (1)$$

where, $C_0$ and $C_e$ is initial and final concentration of dyes (mg/L), V is the volume of solution (L), and m is the mass of adsorbent (g).

## Results and discussion

### *Adsorbent characterization*

Initially, raw sugarcane bagasse appeared in pale yellow, but turned black and became more fragile after being pyrolyzed at 600 °C under $N_2$ atmosphere as shown in Figure 1 a and b. Observation on scanning electron microscope showed that sugarcane bagasse has multiple nano pores on its structure (Figure 1c) and thin layers are sometimes exfoliated from bulk. Upon

https://doi.org/10.62239/jca.2024.069

pyrolysis, the majority of its structure turned to flake-like and honeycomb-like structures (Figure 1 d and e). The honeycomb-like structures contain porous channels in round or oval shapes having diameter or width ranging from about 1 to 3 μm. According to previous studies, fibrous components such as lignin, hemicellulose, and cellulose in sugarcane bagasse undergo different reaction processes such as fragmentation and depolymerization. These processes generate highly porous biochar with variety of functional groups which are adsorptive sites on the biochar's surface [9, 10]. The structure of biochar was well preserved after modification and dye adsorption as exhibited in Figure 1f. Previous works indicated that the surfactant modification may alter the surface charge of biochar and therefore improve its adsorption ability [19, 20].

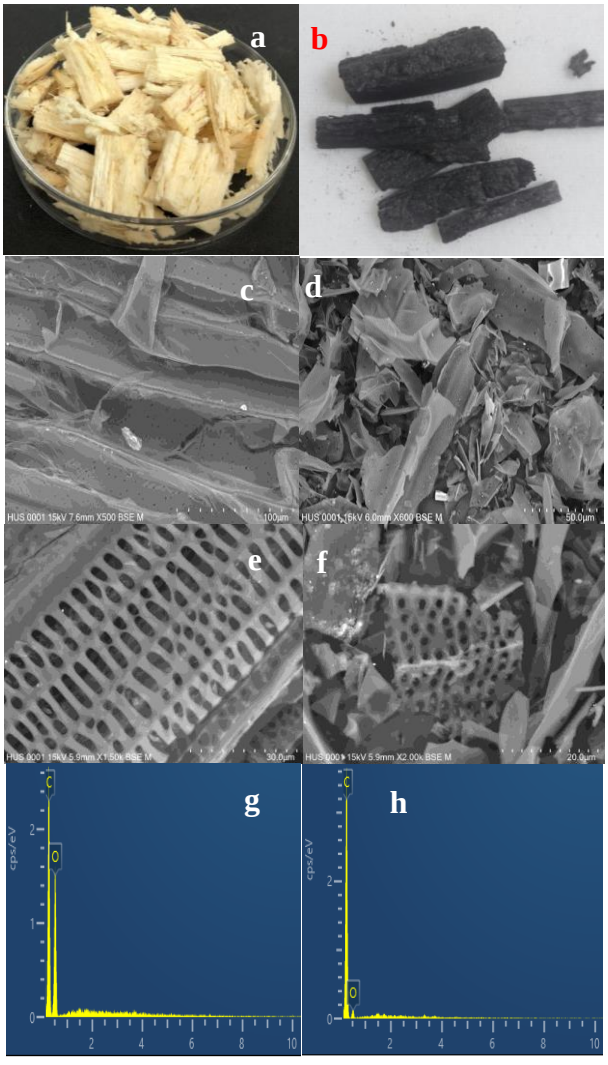


Figure 1: Photos of sugarcane bagasse (a) and biochar (b); SEM images of sugarcane bagasse (c), biochar (d), SDS modified biochar (e), and SDS modified biochar after MB adsorption (f), and EDX spectra of sugarcane bagasse (g) and biochar (h).

Elemental analysis by EDX (Figure 1 g and h) revealed that sugarcane bagasse contains mainly carbon and oxygen, about 52,77 wt% and 47,23 wt%, respectively. The carbon and oxygen contents, however, changed significantly after pyrolysis, in which, carbon increased to 87,72 wt% while oxygen reduced to 12,28 wt%. This variation is likely due to the release of water and volatile components together with the decomposition of biomass at high temperature. This indicated that sugarcane bagasse was carbonized to form biochar. Experimental data showed that the biochar recovered from sugarcane bagasse reached an average efficiency of 24.25 wt%. After modification, EDX analysis showed the presence of sulfur element with a content of about 0.3 wt%. This indicated that SDS molecules were deposited on the BC during modification.

### *Adsorption study*

The adsorption ability of BC and SDS modified BC was investigated with MV dye. Figure 2 shows the relation between removal efficiency and adsorbed amount with adsorption time. The adsorption of MV on BC occurred rapidly; it was almost completed in 60 min. The adsorption rate, however, was further enhanced with SDS modification. As seen in Figure 2, the adsorption on SDS modified BC was rapid at first 5 min and nearly reached maximum adsorption after 15 min for BC modified with the SDS solution of 0.3 and 0.4 g/L. It is likely that the affinity between MV and BC increased due to SDS modification, which resulted in rapid adsorption. Besides, the removal efficiency and adsorption capacity of BC were improved upon the SDS modification. Removal efficiency by BC was 64.16% but it increased to 68.85%, 79.40%, 94.05%, and 97.71% for BC modified with SDS solution of 0.1, 0.2, 0.3, and 0.4 g/L, respectively. Similar to removal efficiency, MV adsorbed amount also increased with concentration of SDS. It was 6.41 mg/g for BC and increased to 9.77 mg/g as BC was treated with SDS solution 0.4 g/L.

According to previous studies, the treatment with SDS may create a layer of surfactant or a local of bilayer in form of admicelles on the surface of adsorbent [19, 20]. The formation of surfactant layer depends on the concentration of surfactant and the nature of adsorbent's surface. For the positive charge surface, the adsorption of SDS may form admicelles and resulted in conversion of surface charge [19]. The hydrophobic sites on surface of adsorbent can interact with hydrophobic tale of surfactant which create single layer with ionic tale outward for adsorption [21]. In this study, the adsorption ability of BC increased significantly with SDS modification. This indicated that the modification does

https://doi.org/10.62239/jca.2024.069

not only improve the affinity between adsorbent and dye molecules but also increase the density of adsorptive sites on it. This demonstrated that the SDS modification resulted in positive effect on the adsorption performance of BC.

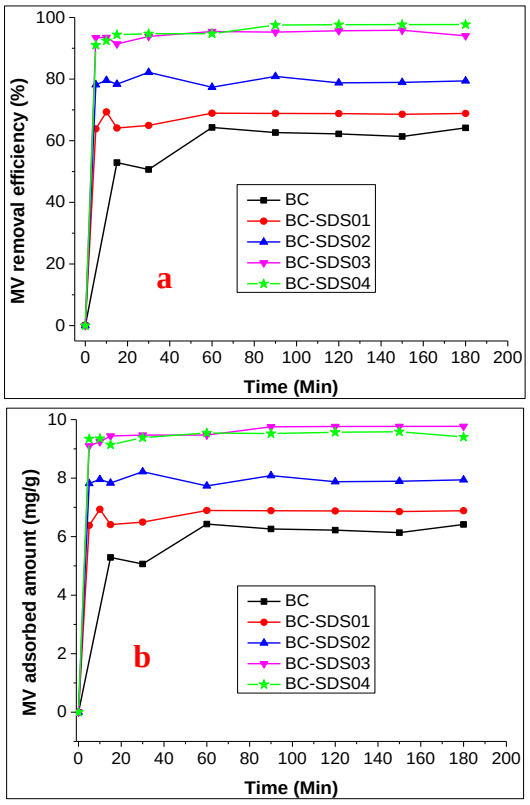


Figure 2: Variation in MV removal efficiency (a) and adsorbed amount (b) as a function of adsorption time (adsorbent dose = 5 g/L, dye concentration = 50 mg/L, and pH ~7.0).

To understand the adsorption mechanism of MV onto BC and modified BC, the linear fitting of equilibrium data to Langmuir and Freundlich isotherm models was investigated. The linear forms of these two models are shown in equation (2) and (3).

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2)$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

where $q_m$ (mg/g) is the maximum adsorption capacity determined from Langmuir model and b is the binding constant relating to the heat of adsorption, $k_f$ and n are the Freundlich constants.

Linear fitting plots of these two models are exhibited in Figure 3 and fitting parameters are given in Table 1. The results showed that the adsorption MV onto both BC and modified BC fits well to Langmuir isotherm model with the regression coefficient ($R^2$) ranging from 0.971 to 0.979. Meanwhile, $R^2$ values for Freundlich isotherm models are from 0.779 to 0.969. The better fitting to Langmuir isotherm model recommended that the interaction between adsorbates and adsorbents are based on chemisorption. One adsorbate molecule presumably interacts with one adsorptive site to from homogenous single adsorption layer. It is likely that the hydrophobic tale of SDS interacts with hydrophobic carbon chain in biochar structure leaving positive charge ionic sulfate tale as surface functional group. The sulfate group in addition to free functional group on previously existed on BC surface can interact with MV molecules resulting in the adsorption.

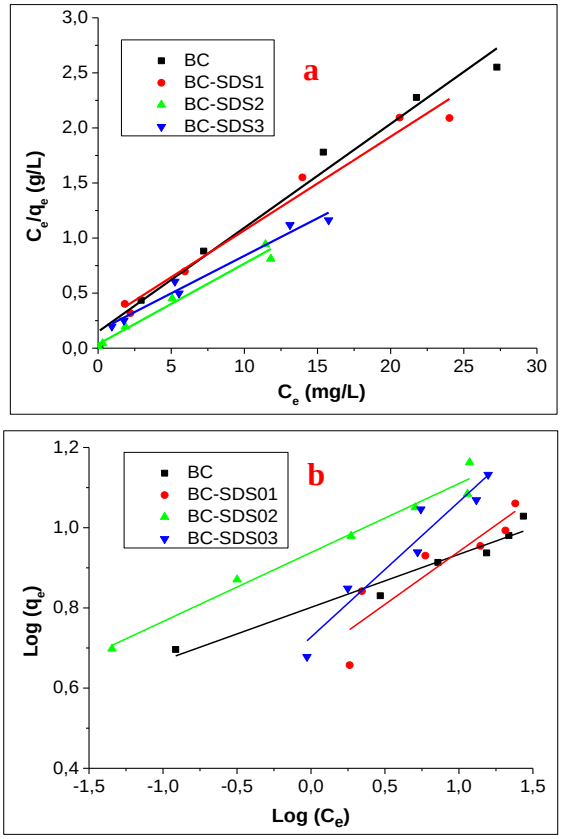


Figure 3: Linear fitting to Langmuir isotherm model (a) and Freundlich isotherm model (b) for MV adsorption

To further demonstrate the adsorption favorability of the adsorption process, parameters received from Langmuir model were used to calculate the dimensionless separation factor $R_L$ according to equation (4). $R_L$ values can be used to evaluate the favorability of adsorption process based on the following rules, i.e. adsorption is favorable with $0<R_L<1$, irreversible with $R_L=0$, linear if $R_L = 1$, and unfavorable when $R_L>1$.

$$R_L = \frac{1}{(1+b.C_0)} \quad (4)$$

where $C_0$ (mg/L) is the highest initial concentration of adsorbates.

https://doi.org/10.62239/jca.2024.069

Table 1: Linear fitting parameters for Langmuir and Freundlich models

| Adsorbents | Langmuir | | | | Freundlich | | |
|---|---|---|---|---|---|---|---|
| | $q_{max}$ (mg/g) | $R^2$ | b (L/mg) | $R_L$ | 1/n | $R^2$ | $k_f$ |
| MV adsorption | | | | | | | |
| BC | 10.59 | 0.979 | 1.580 | 0.009 | 0.1324 | 0.943 | 6.328 |
| BC-SDS01 | 11.75 | 0.973 | 2.578 | 0.006 | 0.2636 | 0.779 | 4.753 |
| BC-SDS02 | 13.66 | 0.974 | 0.495 | 0.028 | 0.1721 | 0.969 | 8.669 |
| BC-SDS03 | 14.68 | 0.971 | 2.314 | 0.006 | 0.3376 | 0.912 | 5.334 |

Calculated $R_L$ ranging from 0.006 to 0.028 (Table 1) means that MV adsorption onto BC and SDS modified BC is a favorable process. Since Langmuir model fits the adsorption data, the maximum adsorption capacity ($q_{max}$) of adsorbents can be calculated from fitting plots. As seen in Table 1, $q_{max}$ values of MV adsorption on BC was 10.59 mg/g, which then increased to 11.75, 13.66 and 14.68 mg/g for BC-SDS01, BC-SDS02, and BC-SDS03, respectively. These equal to 10.95%, 28.99%, and 38.62% improvement in adsorption capacity. These results further confirmed that the modification of BC with SDS can enhance the MV adsorption capacity of sugarcane bagasse derived biochar.

Pseudo first and second order kinetic models were first used to investigate the adsorption kinetics of MV on adsorbents. Linear fitting of experimental data to these models are given in equations (5) and (6), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (6)$$

where $k_1$ and $k_2$ are rate constants for pseudo first and second order kinetic models, respectively.

Results in Figure 4 exhibited that the adsorption showed better fits to pseudo second order kinetic model with $R^2$ values reached 0.999 for both BC and BC-SDS04 samples. The rate constant for BC and BC-SDS04 were 0.077 and 0.1661 (g/mg·min). This indicated that the SDS modification does not only improve the adsorption capacity but also enhance the adsorption rate. Even though $R^2$ values are high for second order kinetic model fitting, it may not always describe accurately the adsorption. Previous studies showed that $R^2$ may not be sensitive enough to distinguish the differences [22]. Therefore, to evaluate the appropriateness of the proposed kinetic model, nonlinear chi-square test ($\chi^2$, equation 7) was used to judge the data calculated based on the pseudo second order kinetic model in comparison with experimental data. Small $\chi^2$ value indicates high similarity between calculated data and experimental data [23].

$$\chi^2 = \sum_{1=1}^{n} \frac{(q_{exp} - q_{cal})^2}{q_{exp}} \quad (7)$$

where, $q_{exp}$ and $q_{cal}$ are experimental adsorbed amount and adsorbed amount calculated based on pseudo second order kinetic model.

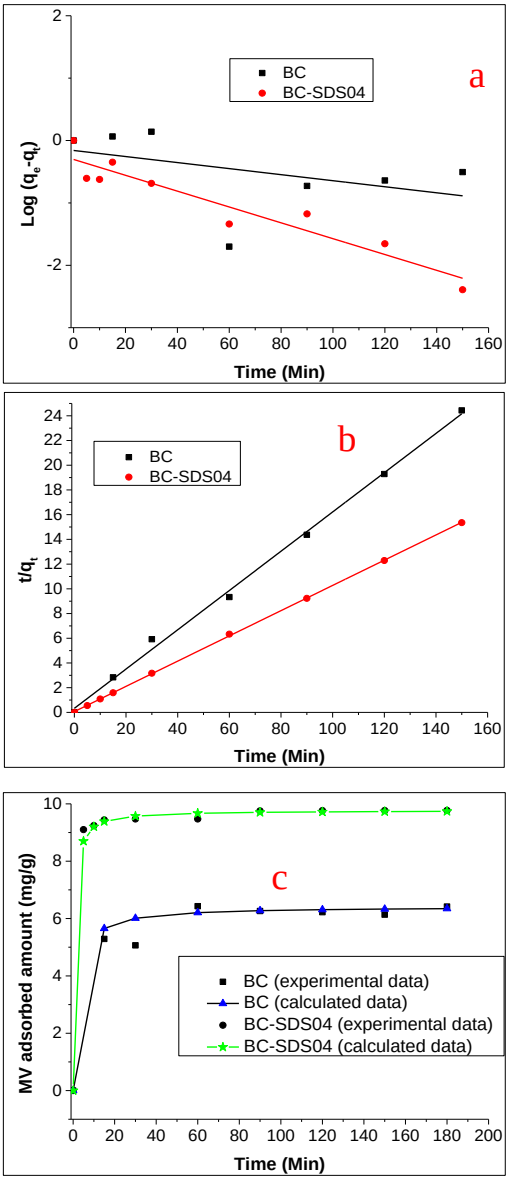


Figure 4: Linear fitting to pseudo first (a), second (b) order kinetic models, and the adsorbed amount calculated based on second order kinetic model (c).

The adsorption progress based on experimental data and predicted data (based on pseudo second order kinetic model) are presented in Figure 4 c. The obtained results indicated that predicted data were close to

experimental data with $\chi^2$ values of 0.047 and 0.024 for BC and BC-SDS04, respectively. These values suggested that the calculated data were similar to experimental ones. These results further confirm the goodness of pseudo second order kinetic model and therefore this model could be used to predict the MV adsorption on sugarcane bagasse biochar.

## Conclusion

In conclusion, the adsorption capacity of BC can be enhanced significantly with SDS modification. Maximum adsorption capacity against MV increased 28.9% as BC was treated with SDS solution 0.4 g/L. The modification also improved the adsorption rate of MV on BC; rate constants increased from 0.067 to 0.161 (g/mg·min). The adsorption of MV on BC and SDS modified BC fitted well to Langmuir model. This indicated that the adsorption mechanism is not changed after modification. The success of this study may provide a facile and coeffective method for modification of agricultural waste derived biochar for environmental application.

## Acknowledgments

This research is funded by Phenikaa University under grant number PU2023-1-A-12.

## References

1. N. Jagadeesh, B. Sundaram, Journal of Hazardous Materials Advances, 9 (2023) 100226. https://doi.org/10.1016/j.hazadv.2022.100226
2. R. Madadi, K. Bester, Marine Pollution Bulletin, 166 (2021) 112247. https://doi.org/10.1016/j.marpolbul.2021.112247
3. L. Ton-That, H.D. Pham, T.N.L. Huynh, B.N. Duong, T.T. Luu, D.K. Nguyen, N.A. Nguyen, T.H. Ho, V.H. Pham, V.P. Dlnh, Vietnam Journal of Catalysis and Adsorption, 12(1) (2023) 1–7. https://doi.org/10.51316/jca.2023.001
4. C. Sun, T. Chen, Q. Huang, J. Wang, S. Lu, J. Yan, Environmental Science and Pollution Research, 26 (2019) 8902-8913. https://doi.org/10.1007/s11356-019-04321-z
5. S.S. Suryawanshi, P.P. Kamble, R. Gurav, Y.H. Yang, J.P. Jadhav, Biomass Conversion and Biorefinery, 13 (2023) 5353–5366. https://doi.org/10.1007/s13399-021-01636-1
6. H.M. Jang, E. Kan, Bioresource Technology, 284 (2019) 437–447. https://doi.org/10.1016/j.biortech.2019.03.131
7. USDA, Sugar: World Markets and Trade, United States Department of Agriculture, Foreign Agricultural Service
8. D.A. Cerqueira, G. Rodrigues Filho, C. da Silva Meireles, Carbohydrate Polymers, 69(3) (2007) 579–582. https://doi.org/10.1016/j.carbpol.2007.01.010
9. K.O. Iwuozor, E.C. Emenike, J.O. Ighalo, F.O. Omoarukhe, P.E. Omuku A.G. Adeniyi, Cleaner Materials, 6 (2022) 100162. https://doi.org/10.1016/j.clema.2022.100162
10. M.K. Zafeer, R.A. Menezes, H. Venkatachalam, K.S. Bhat,. Emergent Materials, 7 (2024) 133–161. https://doi.org/10.1007/s42247-023-00603-y
11. M. Inyang, B. Gao, W. Ding, P. Pullammanappallil, A.R. Zimmerman, X. Cao, Separation Science and Technology, 46(12) (2011) 1950–1956. https://doi.org/10.1080/01496395.2011.584604
12. G. Prasannamedha , P. Senthil Kumar , R. Mehala , T.J. Sharumitha , D. Surendhar, Journal of Hazardous Materials, 407 (2021). 124825. https://doi.org/10.1016/j.jhazmat.2020.124825
13. Y. Qu, L. Xu, Y. Chen, S. Sun, Y. Wang, L. Guo, Environmental Science and Pollution Research, 28 (2021) 62616–62627. https://doi.org/10.1007/s11356-021-15128-2
14. X. Mi, G. Li, W. Zhu, L. Liu, Journal of Chemistry, 2016(1) (2016) 8457030. https://doi.org/10.1155/2016/8457030
15. Y. Li , Y. Wei , S. Huang , X. Liu , Z. Jin , M. Zhang , J. Qu, Y. Jin, Journal of Molecular Liquids, 269 (2018) 824–832. https://doi.org/10.1016/j.molliq.2018.08.060
16. C. Li, Y. Gao, A. Li, L. Zhang, G. Ji, K. Zhu, X. Wang, Y. Zhang, Environmental pollution, 254 (2019) 113005. https://doi.org/10.1016/j.envpol.2019.113005
17. W. Que, L. Jiang, C. Wang, Y. Liu, Z. Zeng, X. Wang, Q. Ning, S. Liu, P. Zhang, S. Liu, Journal of Environmental Sciences, 70 (2018) 166–174. https://doi.org/10.1016/j.jes.2017.11.027
18. N. Zhao, X. Yang, J. Zhang, L. Zhu, Y. Lv, Materials, 10(10) (2017) 1119. https://doi.org/10.3390/ma10101119
19. Pham, T.D., et al., Journal of Molecular Liquids, 287 (2017) 110900. https://doi.org/10.1016/j.molliq.2019.110900
20. Tien Duc Pham , Thi Thuy Tran , Van Anh Le , Thu Thao Pham , Thi Huong Dao , Thanh Son Le, Journal of Chemistry, 2017(1) (2017) 1986071. https://doi.org/10.1155/2017/1986071
21. M. Gęca, A. M. Khalil, M. Tang, A. K. Bhakta, Y. Snoussi, P. Nowicki, M. Wiśniewska, M.M. Chehimi, Surfaces, 6(2): (2023) 179–213. https://doi.org/10.3390/surfaces6020013
22. Y. Liu, L. Shen,. Langmuir, 24(20) (2008) 11625–11630. https://doi.org/10.1021/la801839b
23. K.Y.Foo, B.H. Hameed, Chemical Engineering Journal, 156(1) (2010) 2-10. https://doi.org/10.1016/j.cej.2009.09.013