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

https://jca.edu.vn

Synthesis and characterization of copper loaded activated carbon nanocomposite: Adsorption of Rhodamine B in aqueous solution

Tran Van Anh[1], Nguyen Duc Trung[1], Nguyen Ngoc Tue[1,*]

[1] *Department of Chemistry, School of Chemistry and Life Sciences , Hanoi University of Science and Technology, Hanoi, VIETNAM*
** Email: tue.nguyenngoc@hust.edu.vn*

ARTICLE INFO

Received: 04/08/2024
Accepted: 05/12/2024
Published: 30/03/2025

Keywords:
Carbon; copper; dyes; adsorption; porous

ABSTRACT

The study examined the adsorption of methylene blue from an aqueous solution using activated carbon-loaded copper nanocomposites (Cu@AC). The activated carbon was obtained from Acacia Crassicarpa bark. The Cu@AC were synthesized using a thermal treatment, with a focus on minimizing the time required and assuring an environmentally-friendly and sustainable approach. The Cu@AC nanocomposites underwent characterization using XRD, SEM, EDX, and FTIR techniques. Subsequently, they were subjected to tests to determine their adsorptionisotherm and the impact of experimental factors on the removal of RhB from an aqueous solution. Monolayer adsorption of Rhodamine B was determined to be favorable, with a maximum adsorption capacity of 47.85 mg/g at a temperature of 298 K. The results demonstrate that the Cu@AC nanocomposite may be effectively used as a highly efficient adsorbent for large-scale wastewater treatment.

Introduction

Increased human dependence on water has led to a global shortage of drinkable water, rising consumption, and pollution, creating a gap between fresh water demand and supply. Contaminated drinking water contributes significantly to deaths from diarrheal diseases annually. Biofilms formed by aquatic diseases protect pollutants, necessitating various contaminant removal methods [1-3]. Activated carbon is favored for its cost-effective and efficient filtration. Excessive water consumption and dye use in industries like textiles and pharmaceuticals result in vibrant waste, harming aquatic life, agriculture, and human health. Strict environmental laws demand effective wastewater color removal, making adsorption the most cost-effective and eco-friendly method. Activated carbon, with its large surface area and porosity, is ideal for this purpose but is expensive to produce. Research has improved adsorption by integrating metal oxide nanoparticles with activated carbon [4]. Materials like iron oxide and copper oxide enhance adsorption capacity due to additional interaction sites. Activated carbon from biomass sources, such as coconut coir, is widely used for water treatment [5]. Acacia crassicarpa bark, a low-cost biomass, can be converted into valuable activated carbon. This method introduces functional groups and pores for applications in desalination and fluoride removal. Metal-doped activated carbon shows promise in energy storage, catalysis, and water purification due to enhanced surface properties [6-10]. Advanced carbon materials, including metal-organic frameworks, offer effective adsorption for various contaminants.

https://doi.org/10.62239/jca.2024.003

Additionally, there is scope for developing green synthesis methods to prepare efficient adsorbents with synergetic effects to meet the requirements of wastewater treatment effectively. Consequently, present study was aimed at utilizing Acacia Crassicarpa bark to prepare activated carbon by simple, low-temperature method in minimum possible time duration. The activated carbon-based copper nanocomposites (Cu@AC) were prepared by facile, in-situ synthesis method at room-temperature for the adsorptive removal of RhB dye from aqueous solution. All the reactions in both procedures were carried out at low-temperature and shortest possible duration which ensure their cost-effectiveness and economic feasibility. The adsorption characteristics have been investigated in term of kinetics and thermodynamics to elucidate its mechanism. This study presents a new and simple approach for synthesizing copper nanoparticle doped activated carbon (Cu@AC) through an in-situ reduction method. The study also examines the effectiveness of Cu@AC in purifying drinking water by removing hardness and fluoride, as well as its ability to inhibit the growth of common waterborne pathogens. This study thus explores using Acacia crassicarpa bark to prepare activated carbon-based copper oxide nanocomposites for efficient dye removal and water purification, presenting a cost-effective and environmentally friendly approach.

Experimental

Materials required

The chemicals used in the experiment were copper sulphate ($CuSO_4.5H_2O$; 99.99%), oxalic acid (≥ 99%), sodium hydroxide (96.4%), and Rhodamine B($C_{28}H_{31}N_2O_3.Cl$). These chemicals were procured from Xilong Inc, and were used as received without any additional purification. The barks were gathered from the Nghe An province in Vietnam. They were then cleaned and rinsed with distilled water. After that, they were dried in an oven at a temperature of 130 °C for one hour. These dried barks were then used to create activated carbon using the following method.

Preparation of Activated Carbon

The desiccated pods of Acacia crassicarpa bark were fragmented into small fragments and subjected to combustion on an electric heating element for a duration of 5 minutes at a temperature of 180 °C, resulting in their transformation into charcoal. The charcoal was pulverized into a fine powder using a mortar and pestle, and then made uniform by utilizing a motorized automatic sieve shaker with a capacity of approximately 40 mesh size, resulting in exact particles. The processed coal was moved to a sterile sample container for preservation. To activate the charcoal, 1 gram of P. juliflora biochar was combined with 100 milliliters of a 3.74 molar aqueous solution of KOH. The mixture was stirred for 24 hours and then filtered under vacuum. The powder was then went through the procedure described in the previous study [4,5].

The Cu@AC (activated carbon) nanocomposite was synthesized in-situ as following: First, a homogeneous carbon dispersion was formed by ultrasonication of 10 mg of activated carbon in 10 mL of deionized water for 2 hours at room temperature. A solution containing 20 millimoles of $CuSO_4$ was combined with the dispersion while maintaining continuous stirring. A solution containing 40 millimoles of oxalic acid was added to the mixture mentioned above as a reducing agent. The combination was agitated consistently for a duration of 30 minutes till the color of the solution transitioned to black, signifying the creation of Cu@AC nanocomposites. The precipitates were subjected to centrifugation at a speed of 3000 revolutions per minute. They were then cleansed with distilled water and ethanol, and subsequently dried at a temperature of 60 °C for a duration of 2 hours. Finally, the material underwent thermal treatment in a programmed furnace while being exposed to a flow of Argon gas at a rate of 30 mL per minute. The ideal preparation conditions for Cu@AC were as follows: a temperature of 550°C, a heating rate of 5°C.min^{-1}, and an impregnation period of 2 hours.

Analysis of the fabricated nanocomposite's characteristics

The structure of the synthesized molecule was determined by performing X-ray diffraction (XRD) analysis using a Bruker X-ray diffractometer, namely the D8 DISCOVER model. The study was conducted in the range of 10° to 80°. The nanocomposite's surface morphology was acquired using a scanning electron microscopy (SEM).

Adsorption experiment

Each experiment has been repeated four times to make sure the repeatability and reliability. Concentrations of the dyes were estimated using the linear regression equations (obtained by plotting its calibration curve). The amount of adsorbed the two dyes by adsorbent (q_e (mg/g)) was calculated by the following equation

https://doi.org/10.62239/jca.2024.003

$$q_e = \frac{(C_o - C_e)V}{W}$$

where Co and Ce are the initial and equilibrium concentrations of the adsorbates (in this case RhB), respectively. V represents the volume of the solution in liters, whereas M is the weight of the adsorbent in grams. The adsorption equilibrium features of RhB on the activated and carbon-based materials were evaluated using the Freundlich and Langmuir isotherm models.

Results and discussion

Initially, the morphological and structural features of the Cu-ACC were studied to establish structure-property relationships. The morphological characteristics of Cu-ACC observed in Scanning Electron Microscopy (SEM) are shown in Fig 2. The SEM images show the effective integration of metal particles onto the activated carbon surface. The photos in the top-left and bottom-right illustrate areas with more uniform and compact structures, suggesting the presence of metallic deposits, presumably copper, dispersed within the carbon matrix. The porous and abrasive texture of the activated carbon, illustrated in the top-right and bottom-left photos, offers an extensive surface area, promoting the adhesion and distribution of the metal. The linked and porous structure guarantees consistent metal distribution while preserving the inherent porosity of the activated carbon, which is crucial for applications such as adsorption, catalysis, or electrochemical processes. The observed morphological variation indicates localized metal deposition, likely affected by synthesis conditions, while the porosity portions show the material's appropriateness for improved surface interaction. Additional characterisation techniques, such as EDS mapping or elemental analysis, would verify the distribution and concentration of the metal within the carbon matrix. Thus, the darker spots observed in the SEM image indicate the presence of Cu nanoparticle within the activated carbon matrix, and they have spherical shapes with less than 5 nm of the average diameter. It is evident that Cu nanoparticles have grown in a non-uniform morphology with clustered agglomerates. Cu nanomaterial shave particle sizes ranging from a few nanometers to several micrometres. On the other hand, the SEM images clearly depicts that combining with activated carbon, Cu particles have scattered themselves over the surface of activated carbon with strong binding.

XRD study

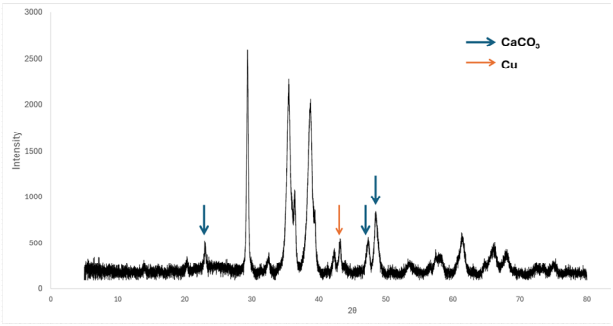

Fig. 1. XRD pattern of Cu@AC materials. The blue arrow indicate the peaks corresonding to the presence of $CaCO_3$ while the other ones coresponding to the presence of Cu

Error! Reference source not found. represents the X-ray diffraction images of CuO@AC nanocomposite. The X-ray diffraction (XRD) pattern confirms the existence of two crystalline phases: copper (Cu) and calcium carbonate ($CaCO_3$). The prominent peaks belong to metallic Cu, seen at around 43.54°, 50.50°, and 74.10°, signifying its elevated crystallinity. The peaks corresponding to $CaCO_3$, indicated by blue arrows, signify an impurity phase, exhibiting reflections at approximately 29.4° and 47°. The pronounced peaks imply high crystallinity, but the subdued background signifies limited amorphous material. The presence of $CaCO_3$ as an impurity indicates it may have been introduced during synthesis or sample preparation. The main diffraction peaks at 43.54 in the pattern mark the signature pattern of crystal structure of Cu. These findings have good corroboration with the standard pattern of Cu (JCPDS-80-1268) and literatures. Its wide diffraction peak pattern indicates that activated carbon is amorphous which makes it an ideal substrate for formation of the nanocomposite materials. The intensity reflection of activated carbon has been found to decrease due to *in-situ* synthesis of nanocomposite These results confirm that nanocomposite has been successfully synthesized under given experimental conditions. The average crystallite size was determined using Debye-Scherrer equation from the main intensity peaks and was found to be 28 ± 1 nm. Signature peaks of metal and activated carbon confirm the successful synthesis of Cu loaded with activated carbon. It is noteworthy that both the intensity and width of the peak assigned to hydroxyl groups have changed in the nanocomposite, which probably explains the surface hydroxyl groups of copper. The AC and Cu@AC showed a S_{BET} of 543.56 $m^2\ g^{-1}$ and 792.65 $m^2\ g^{-1}$, an average value.

https://doi.org/10.62239/jca.2024.003

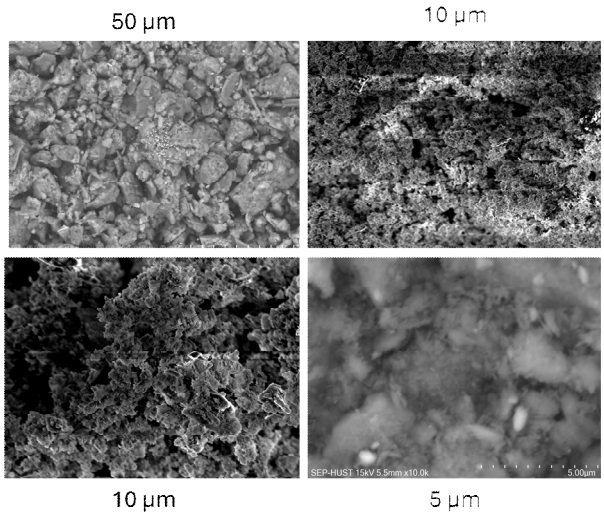

Fig 1. The SEM image at different magnifications

The adsorption ability of as-synthesized Cu@AC nanocomposite was compared with activated carbon by taking 0.1 g of each adsorbent for the removal of 10 to 20 mg/L RhB at room temperature and neutral pH. The adsorbent dosage is a paramount factor which strongly affects the extent of adsorption on the surface of adsorbent. Fig 3 and Fig 4 clearly demonstrate the relationship of adsorbent amount with adsorption capacity; the absorbance of RhB solution gradually increases linearly with increasing the amount of RhB concentration at 298 K. The Langmuir adsorption isotherm shown in the figure demonstrates a strong correlation to the model, with a high R^2 value of 0.9886. From the linear equation, the maximum adsorption capacity (q_{max}) of 47.85 mg/g, indicating significant adsorption potential. The linear nature of the plot confirms that the adsorption process adheres to Langmuir assumptions, involving monolayer adsorption on a uniform surface with consistent active sites. This validates the material's suitability for applications such as pollutant removal. Additional analysis, such as calculating K_L and comparing with other isotherm models, could provide further insight into the adsorption behavior and material properties.

All R_L values were determined to be less than 1 (0.1–0.5) which confirms that the adsorption of MB is favorable to the Cu@AC nanocomposite under the specific experimental circumstances used in this investigation. Conversely, the lower values of R^2 for the Freundlich isotherm compared to the Langmuir isotherm indicate a lack of fit of the experimental data. The results of this investigation confirm that the Langmuir isotherm is the most accurate model for describing the adsorption of RhB over the Cu@AC nanocomposite.

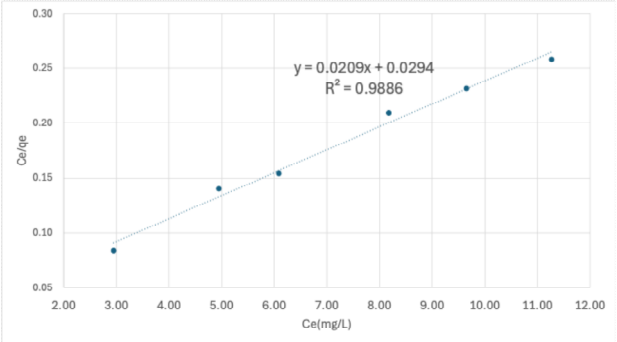

Fig 2. Langmuir adsorption isotherm for RhB removal using Cu@AC materials

The graph in Fig 5 shows the adsorption kinetics, illustrating the ratio of remaining concentration to beginning concentration over time. A quick decline in this ratio is noted during the initial 30 minutes, signifying rapid initial adsorption, presumably attributable to the presence of many active sites on the adsorbent surface. Beyond this juncture, the adsorption rate diminishes and stabilizes between 120 and 150 minutes, indicating that the adsorption process nears equilibrium. The data indicates that the material exhibits significant adsorption efficiency, with the majority of the adsorbate eliminated in a brief period.

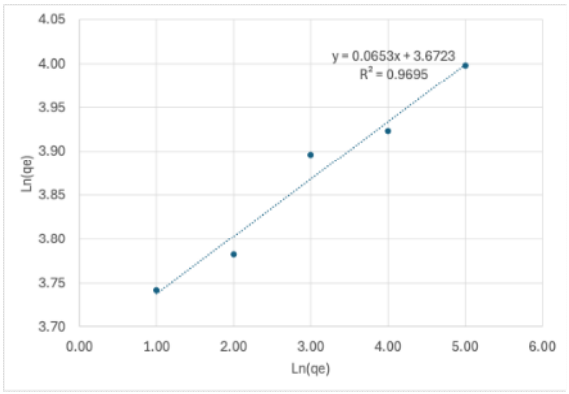

Fig 3. Freudlinch adsorption isotherm for RhB removal using Cu@AC materials

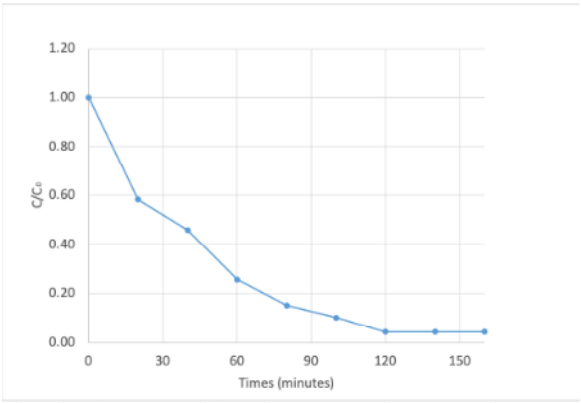

Fig 5. Adsorption isotherm kinetics for RhB removal using Cu@AC materials

https://doi.org/10.62239/jca.2024.003

Conclusion

The Acacia crassicarpa bark, was used to create activated carbon via the thermal treatment. This activated carbon was then used to build an integrated adsorbent. Cu@AC nanocomposites were effectively synthesized using a simple in-situ approach at room temperature, with the purpose of later using them to remove RhB from an aqueous solution. The thorough material characterization uncovered the creation of a singular-phase monoclinic copper that was infused with activated carbon, resulting in a porous surface. The highest amount of RhB was absorbed at a pH close to neutral, about 47.85 mg/g, the potential values for evaluating the adsorbates. The adsorption process primarily involves electrostatic charge interaction between the negatively charged surface of the Cu@AC nanocomposite and the positively charged polar groups of RhB. The produced nanocomposite demonstrated stability over four repeated adsorption trials. The results indicate that the Cu@AC nanocomposite has great potential as a viable option for treating wastewater.

Acknowledgments

This research is funded by the Hanoi University of Science and Technology (HUST) under project number T2021-SAHEP-016.

References

1. M. Karnib, A. Kabbani, H. Holail, and Z. Olama, Energy Procedia, 50 (2014) 113–120. https://doi.org/10.1016/j.egypro.2014.06.014
2. X. Zheng *et al.*, Sci Rep, 8(1) (2018) 3–11, https://doi.org/10.1038/s41598-018-24891-1
3. L. Largitte, T. Brudey, T. Tant, P. C. Dumesnil, and P. Lodewyckx, Microporous and Mesoporous Materials, 219 (2016) 265–275. https://doi.org/10.1016/j.micromeso.2015.07.005
4. T. N. Nguyen, K. Q. Dang, and D. T. Nguyen, Ministry of Science and Technology, Vietnam, 63(4) (2021) 23–27. https://doi.org/10.31276/VJSTE.63(4).23-27
5. N. D. Trung, T. T. Minh, D. Q. Khanh, and N. N. Tue, Vietnam Journal of Chemistry, 60(4) (2022) 546–551. https://doi.org/10.1002/vjch.202200032.
6. J. H. Park, R. H. Hwang, H. C. Yoon, and K. B. Yi, Journal of Industrial and Engineering Chemistry, 74 (2019) 199–207. https://doi.org/10.1016/j.jiec.2019.03.004.
7. A. R. Silva, M. Martins, M. M. A. Freitas, J. L. Figueiredo, C. Freire, and B. De Castro, Eur J Inorg Chem, 10 (2024) 2027–2035. https://doi.org/10.1002/ejic.200300796.
8. M. Mariana, A. Khalil H.P.S., E.M. Mistar, E.B. Yahya, T. Alfatah, M. Danish, M. Amayreh, Journal of Water Process Engineering, 43 (2021) 102221. https://doi.org/10.1016/j.jwpe.2021.102221
9. I. A. W. Tan, B. H. Hameed, and A. L. Ahmad, Chemical Engineering Journal, 127(1–3) (2007) 111–119. https://doi.org/10.1016/j.cej.2006.09.010.
10. J. Shu, S. Cheng, H. Xia, L. Zhang, J. Peng, C. Li, S. Zhang, RSC Adv, 7(24) (2017) 14395–14405, https://doi.org/10.1039/C7RA00287D