Investigation of the adsorption potential of green coffee husks biochar activated with K_2CO_3 for caffeine removal from water

NGÔ KIM CHI [1]*, NGUYỄN HOÀI LINH[1] , ĐẶNG NGỌC PHƯỢNG [1]
PHẠM PHƯƠNG THẢO [2], TRẦN LÊ MINH[2], ĐỖ THUỶ TIÊN [3]
VŨ PHƯƠNG UYÊN[3], ĐẶNG VĂN HƯNG[4], HOÀNG THỊ THU HƯƠNG[2]
[1]Institute of Natural Products Chemistry, Vietnam Academy of Science and Technology (VAST)
[2]School of Chemistry and Life Science (SCLS), Hanoi University of Science and Technology (HUST)
[3] Hanoi Pedagogical University 2
[4] University of Science – Vietnam National University

Abstract

The abundant coffee by-products in Vietnam have great potential for producing environmentally friendly adsorbent materials, increasing the value of processed coffee products, contributing to climate change mitigation. The objective of this study is to evaluate the microstructure of coffee husk biochar (BC) and potassium carbonate-activated biochar (BC-K_2CO_3) revealed the material has rough surface with numerous pores ranging from 100 nm to 300 nm. When used at a dosage of 0.1 g/mL with an adsorption time of 120 minutes and an initial caffeine concentration below 0.025 g/mL, it achieved an adsorption efficiency of over 89.75%. The kinetic caffeine adsorption of BC-K_2CO_3 aligns well with the Freundlich adsorption isotherm model (R^2 >0.992). BC-K_2CO_3 exhibited a maximum adsorption capacity (Q_m = 33.74 mg/g), significantly higher than the control sample biochar BC (Q_m= 13.99 mg/g), which was produced under the same pyrolysis conditions without K_2CO_3 activation.

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1. INTRODUCTION

Vietnam is the world's leading exporter of Robusta coffee, significantly contributing to the national economy. The coffee processing industry generates coffee husks at a rate of 0.6–0.78 kg of husk per 1 kg of green coffee beans. This husk can be converted into valuable materials, such as ammonium adsorbents, nutrients, fertilizers, cyclic chemicals, inks, aromatic substances, pharmaceuticals (notably caffeine), and adsorbents for caffeine removal from aqueous environments, caffeine-containing extracts, or wastewater. Additionally, there is an increasing demand for safe and effective caffeine adsorbents to produce caffeine-free coffee products, especially for individuals sensitive to caffeine[1-18].

The use of water and activated carbon adsorbents for caffeine removal in decaffeinated coffee production (decaf coffee beans) provides an alternative to traditional methods that rely on environmentally harmful organic solvents. While activated carbon has been widely used for this purpose, the activation of biochar derived from coffee husks in this study presents an opportunity to develop caffeine adsorbents for water treatment as well as for producing high-value caffeine-free coffee extracts. Replacing conventional caffeine removal methods which often use hazardous chemical solvents such as methylene chloride, chloroform, or the less toxic ethyl acetate helps address environmental concerns, chemical residues, and cost issues[1].

Supercritical CO_2 extraction, proposed by Zosel[2], is a more environmentally friendly approach but requires high equipment costs due to the need for high pressure. The use of biochar has emerged as a sustainable and promising solution[3]. Studies such as those by Elvio et al. (2021) have demonstrated the significant caffeine adsorption capacity of activated carbon derived from coconut leaves[4]. Similarly, Keerthanan et al. (2020) highlighted the advantages of biochar derived from pyrolyzed tea plant residues[5].

Our research focuses on utilizing biochar derived from coffee husks activated with K_2CO_3 (BC-K_2CO_3) and comparing it with non-activated biochar (BC). The objective is to develop an environmentally friendly and cost-effective caffeine removal material and method that promotes waste recycling without the use of harmful chemicals[3]. This approach aims to repurpose coffee husks for the selective adsorption of caffeine, contributing to the production of value-added materials from coffee by-products and high-value decaffeinated coffee products. The outcome of this study is the development of a novel, eco-friendly biochar material for caffeine adsorption, offering environmental, economic, and public health benefits while supporting the production of decaffeinated coffee beans.

2. MATERIALS AND METHODS

2.1. Materials

Coffee husk and green coffee bean were collected from Cư M'gar - Dak Lak (Dak Lak – Vietnam).

2.2. Experiments

Preparation of biochar samples

Method 1: Making biochar of coffee husks (BC)

3 grams of green coffee husks were tightly packed into a cup with a lid. Slow pyrolysis was conducted under anaerobic conditions within the cup. The temperature was gradually increased to 400 degrees Celsius and maintained for 30 minutes. This process resulted in the production of BC biochar.

Method 2: Making biochar activated with K_2CO_3 (BC- K_2CO_3)

BC and K_2CO_3 were mixed at a 1:3 mass ratio and allowed to react for 2 hours. Afterward, the reacted sample was tightly packed into a cup with a lid. Slow pyrolysis was then conducted under anaerobic conditions. The temperature was gradually increased at a rate of 10 degrees Celsius per minute until it reached 400 degrees Celsius. This temperature was maintained for 30 minutes. This process resulted in the production of BC-K_2CO_3 biochar.

Method 3: Making caffeine extraction of green coffee beans

The coffee bean was grounded and impregnated with deion water at the rate of 10 mL.g^{-1} with a heating of 80^{o}C for 3 hours. Coffee bean extract was determined at pH = 6.7 and stored at -4^{o}C for further experiments.

Setting up experiments

The influence of contacting time (10-180 minutes) on the treatment efficiency was carried out at the pH of 6.7; biochar dose of 0.05 g.mL^{-1}, agitation of 100 rpm. The influence of the biochar dose (0.01 - 0.15 g.mL^{-1}) on the caffeine removal capacity was carried out at pH of6.7, agitation of 100 rpm for 120 minutes. The influence of initial caffeine concentration on treatment efficiency was carried out at pH of6.7, biochar dose was 0.15 g.mL^{-1}, agitation of 100 rpm for 120 minutes.

Analysis methods: The biochar microstructure was analyzed by SEM technique, The FTIR was done by Bruker Tensor 27 IR (USA) in spectral range from 400 cm^{-1} to 4000 cm^{-1}.[6]

Adsorption isotherm and kinetic model

The caffeine adsorption isotherm of biochar was evaluated by Langmuir (1) and Freundlich (2) models.[7]

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{bQ_m} \quad (1) \qquad q_e = K_F C_e^{\frac{1}{n}} \quad (2)$$

where:q_e (mg.g^{-1}) and C_e (mg.l^{-1}) are equilibrium ammonium ion concentrations in solid phase and liquid phase, respectively; Q_m (mg.g^{-1}) is the maximum adsorption capacity of the material and b(kl.g^{-1}) is the equilibrium constant related to the adsorption energy; K_F and n are Freundlich constants. The adsorption rate is either first-order (3), or second-order (4), dependent on the capacity of the adsorbent.[8]

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \qquad (3)$$

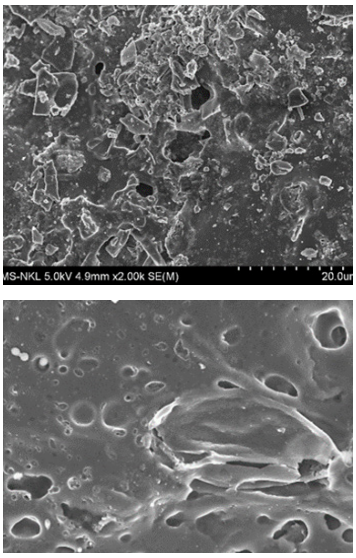
$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}\left(t\right) \qquad (4)$$

where: Q_t (mg.g^{-1}) is adsorption capacity at time t (min), Q_e (mg.g^{-1}) is adsorption capacity at equilibrium time, k_1 (min^{-1}) and k_2 (g.mg$^{-1.}$ min^{-1}) are rate constants.

3. RESULTS AND DISCUSSION

3.1. Characteristics of biochar

The SEM imaging presented in Figure 1 and 2 show that the material has a rough surface, many pores with pore size in the range of 100 nm to 300 nm (BC-K_2CO_3). This feature contributes to the material's good adsorption and retention capacity for pollutants. Thermal treatment at elevated temperatures can induce the decomposition of constituent components such as cellulose and lignin within the material, concurrently leading to an expansion of its pore structure. This phenomenon is associated with an enhanced adsorption efficiency.[8,9,10]

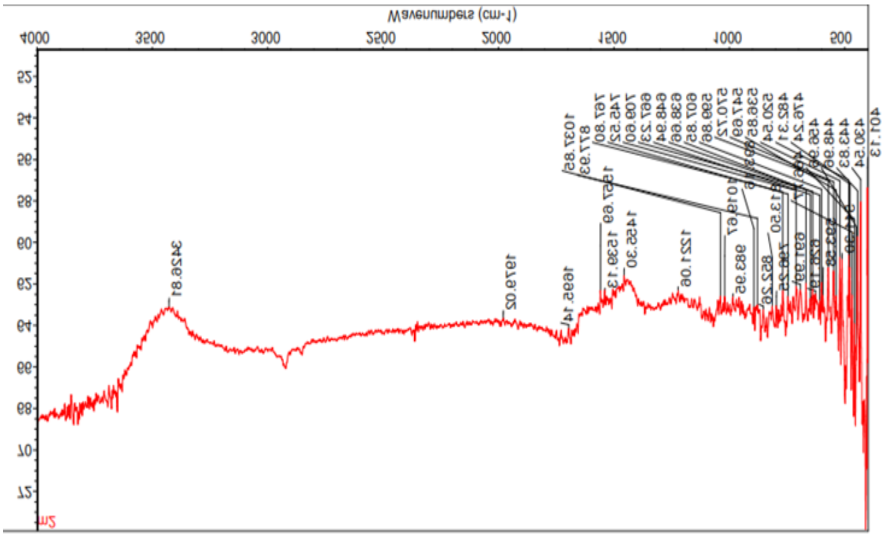


▲ *Figure1: SEM images of BC*

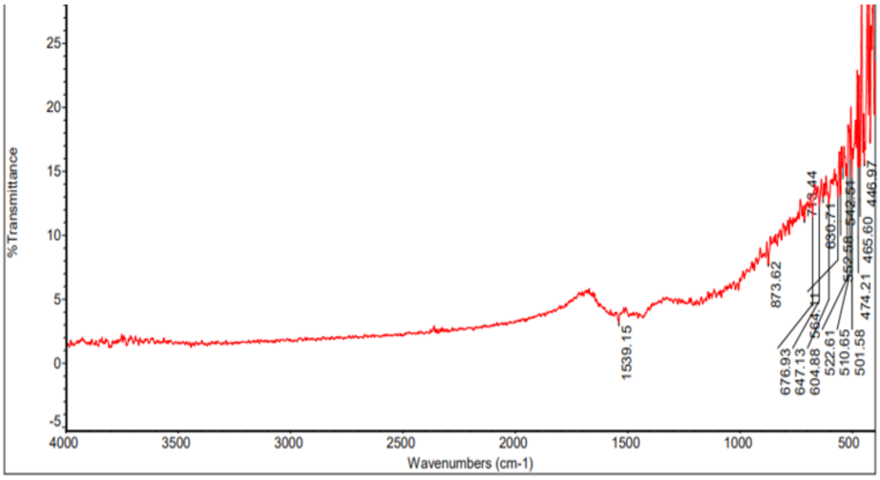
The FTIR spectra (Figure 3 and 4) showed that the functional groups on the surface of the biochars are in the range of 500-4000 cm^{-1}.The wide spectral band in the range of 3500-3000 cm^{-1} of both biochar due to the OH group being stretched and the OH group present in cellulose, lignin, water or can also correspond to the N-H valence oscillation in the amine (first-order and second-order) and carbohydrate groups in macromolecular compounds; the spectral band near the 1500 cm^{-1} value indicates that the C=C bond is stretched in the structure of both biochars; spectral in the range of 1300-1000 cm^{-1} shows the appearance of C-O bond.[11]

3.2 Effect of contacting time on the adsorption

The effect of contacting time on caffeine treatment efficiency was carried out in the time from 10 to 180 min at initial pH 6.7. The Figure 5 resulted that after the first 30 minutes, the adsorption rate increased slowly. Between 30 and 120 min, the adsorption rate continued to increase, then gradually stabilized and reached equilibrium after 120 min in both BC and BC-K_2CO_3, with the treatment efficiency reaching 39.48% and 62.01%. This trend could be explained as follows: the initial rapid adsorption is due to the caffeine replacing the positive ion on the material's surface. In the first time of contact, the biochar has a lot of vacant adsorption sites, the caffeine concentration in the water is the highest, so the adsorption process is high and leads to a rapid increase in the process efficiency. The next slower rising phase represents physical adsorption deterioration with ionic equilibrium. The slow increase is due to chemisorption and diffusion of caffeine inside the material, then reaches saturation of the active sites.[12]



▲ *Figure 3. FTIR spectra of BC-K_2CO_3*



▲ *Figure 4. FTIR spectra of BC-K_2CO_3after caffeine adsorption*

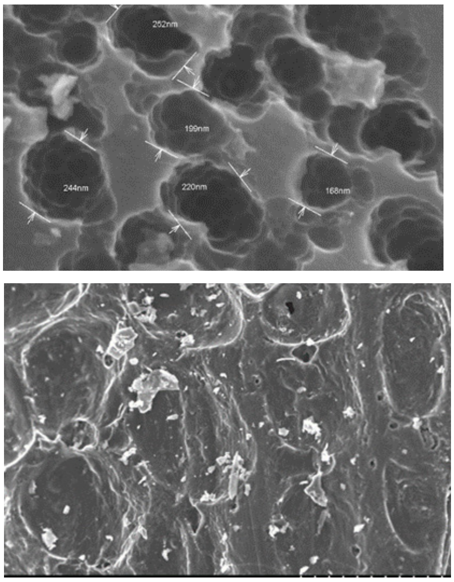
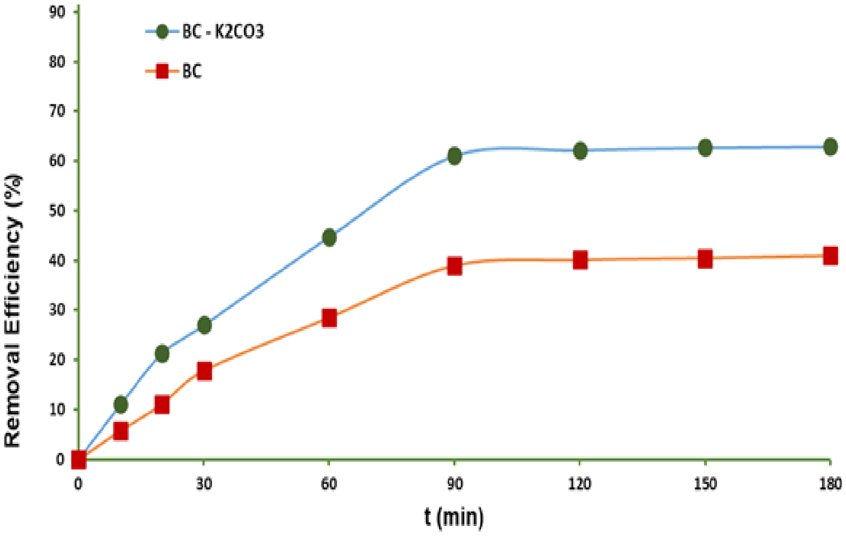


Figure2: SEM images of BC- K_2CO_3

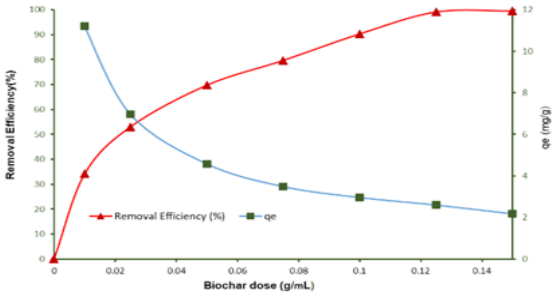


▲ *Figure 5. Effect of contact time on caffeine removal efficiency byBC and BC-K_2CO_3*

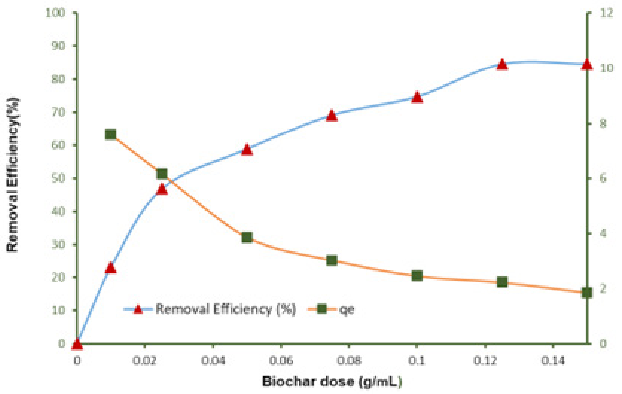
3.3. Effect of biochar on the adsorption capacity

The biochar dosage (g.mL^{-1}) was carried out at pH6.7, contact time was 120 min, there was a change in the ratio between the mass of the material and the volume of the solution in the range from 0.01 to 0.15 g.mL^{-1}. Figure 6a and 6b showed that the caffeine adsorption efficiency increased rapidly from 22.89% to 44.55% for BC and from 31.29% to 53.36% for BC-K_2CO_3 when the biochar dosage was in the range from 0.01 to 0.1 g.mL^{-1}.

For both BC and BC-K_2CO_3, when the biochar dosage increased to 0.15 g.mL^{-1}, the treatment efficiency did not increase too much and the biochar dosage for the highest adsorption efficiency is 0.15g.mL^{-1}. When the material dosage is higher, the contact surface will be larger and more caffeine will be adsorbed on the surface. However, when the biochar dosage was increased to a certain value, the caffeine adsorption was not significantly increased because the overlap of adsorbent layers could obscure the active sites.



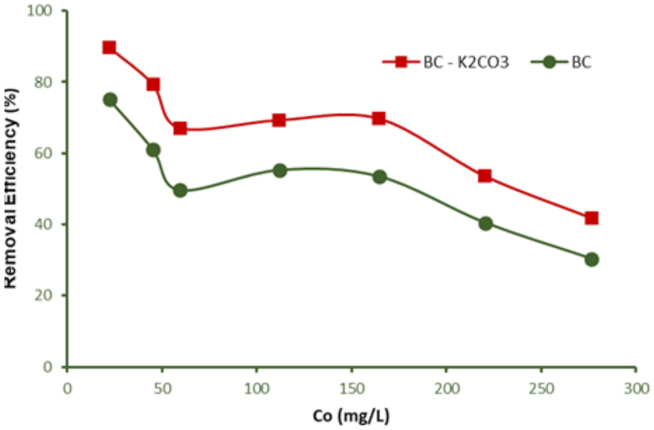
▲ Figure 6a. Effect of biochar dosage on caffeine removal efficiency and amount of caffeine adsorbed on the surface of materials BC-K_2CO_3



▲ Figure 6b. Effect of biochar dosage on caffeine removal efficiency and amount of caffeine adsorbed on the surface of materials BC

3.4. Effect of initial caffeine concentration on the adsorption capacity

To investigate the influence of initial caffeine concentration, experiments were carried out with BC and BC-K_2CO_3 materials at biochar dosage of 0.05 g.mL^{-1}, agitation of 100 rpm for 120 min. The initial caffeine concentration was investigated ranging from 0.02 to 0.27 mg.mL^{-1}. Figure 7 showed that the initial caffeine concentration was 0.02 mg.mL^{-1}, the treatment efficiencies of BC and BC-K_2CO_3 were 75.1% and 89.7%, respectively. With an increase in initial caffeine concentration from 0.02 to 0.27 mg.mL^{-1}, the efficiency decreased from 75.1% to 30.3% with BC and from 89.7% to 41.6% with BC- K_2CO_3. This reduction can be attributed to the limited maximum adsorption capacity of the materials.[13] When the material surface does not have enough adsorbent sites to adsorb caffeine, increasing the concentration of caffeine solution while keeping the same dose of material will cause the amount of free caffeine to increase while the adsorbed caffeine remains unchanged, leading to the adsorption efficiency was gradually reduced.



▲ Figure 7. Effect of initial caffeine concentration on caffeine adsorption efficiency by BC and BC-K_2CO_3

Caffeine adsorption isotherm: The studies of equilibrium in adsorption indicate the biochar adsorption capacity by Langmuir and Freundlich models that have been widely used. The experimental results are shown in Figure 8 and 9, and the constants are shown in Table 1. The suitability between the model and experimental data is shown by the correlation coefficient R^2. The correlation coefficient R^2 in Table 1 shown that caffeine treatment with biochar is more consistent with Freundlich adsorption theory for both materials BC and BC-K_2CO_3 ($R^2$of 0.992 and 0.963).

For the Langmuir theory, the R^2 values of the two materials are both in the range of 0.8 to 0.9. It could be seen that the adsorption of biochar can not only describe the linear or saturation region and the working concentration range. The caffeine adsorbant follows both monolayer and multilayer mechanisms. The caffeine extraction process may not follow a

Table 1: Parameters of Langmuir and Freundlich isotherms and coefficient of determination (R^2) for model

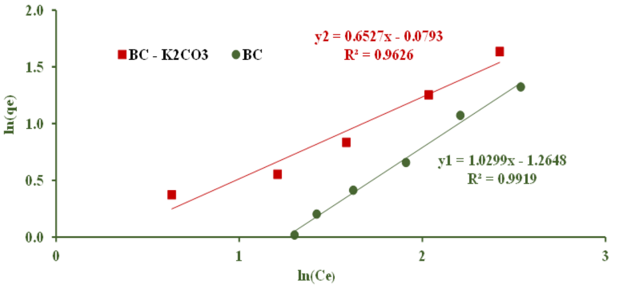
Parameters	Parameter values		R^2	
	BC	BC-K_2CO_3	BC	BC-K_2CO_3
Langmuir			0.864	0.806
b (L.mg^{-1})	0.029	0.015		
Q_m (mg.g^{-1})	13.99	33.74		
Freundlich			0.992	0.963
K (mg.g^{-1})	1.199	1.197		
n	0.834	0.692		

Table 2. Kinetic models applied and parameters and coefficient of determinations (R^2) obtained from the model fits

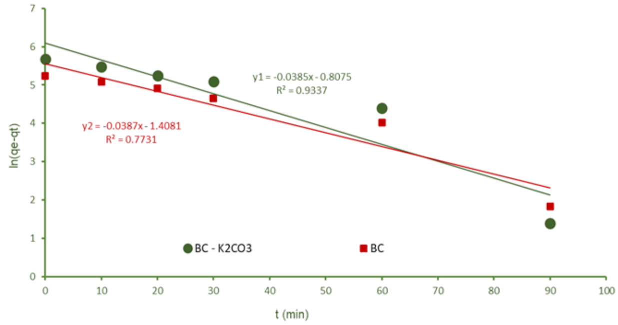
Parameters	**Parameters**		**R^2**	
	BC	**BC-K_2CO_3**	**BC**	**BC-K_2CO_3**
Pseudo-first order			0.934	0.773
k_1 (1.min^{-1})	0.038	0.040		
q_{e1} (mg.g^{-1})	1.48	1.94		
Pseudo-second order			0.999	1
k_2 (g.(mg. min^{-1})	0.624	1.758		
q_{e2} (mg.g^{-1})	1.48	1.94		

single adsorption mechanism, but rather multiple mechanisms (ion exchange, chemisorption, complexation...). Therefore, the use of the Langmuir or Freundlich adsorption theory to describe the adsorption process by the experimental material can only provide an approximate description.

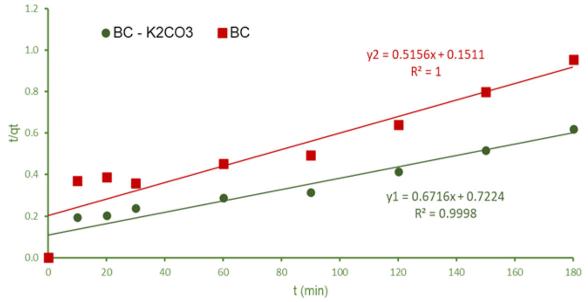
***Caffeine adsorption kinetic*:** Results have been shown in Table 2 and Figure 10 and 11. Table 2 showed that the correlation coefficient R^2 for each material in both pseudo-second-order kinetic models is very high (greater than 0.999). For the BC-K_2CO_3 material, the R^2 value for the second-order model reaches a value of 1. However, the experimental q_e value also needs to be compared with the q_e value calculated from the two models. The second-order model gives q_e value closer to the experimental value. Therefore, it can be concluded that the caffeine treatment process fits the pseudo-second-order kinetic model.



▲ *Figure 9. Freundlich model*



▲ *Figure 10. Pseudo-first-order model prediction of the kinetics of caffeine removal*



▲ *Figure 11. Pseudo-second-order model prediction of the kinetics of caffeine removal*

3.5. Comparison of caffeine adsorption by various adsorbents

Previous studies have investigated the adsorption of caffeine by various adsorbents, including activated carbon, carbon xerogel, and biochars. Activated carbon and carbon xerogel exhibited high caffeine adsorption capacities due to their extensive surface areas.[14,15] However, their production often involves significant use of chemicals and high energy consumption, leading to increased costs. Consequently, there is growing interest in utilizing environmentally friendly waste materials as low-cost alternatives for contaminant remediation.While fique bagasse biochar displayed a caffeine adsorption capacity of 3.52 – 9.13 mg.g^{-1},[16] and woodchip biochar a capacity of 13.2 mg.L^{-1},[17] this study presents a novel approachof using coffee husk activated by K_2CO_3 at suitable temparature 400^{0}C that could be easily made by local biochar maker equipment at local site. We engineered BC-$K_2CO_3$and make the comparison with previously reported, our BC-K_2CO_3 coffee husk biochar activated by K_2CO_3adsorbents caffein with high adsorptioncapacity Q_m = 33.74 mg.g^{-1}.

4. CONCLUSION

In this study, we investigated the adsorption potential of biochar derived from pyrolyzing waste green coffee for caffeine removal. BC-K_2CO_3 exhibited a rough surface and abundant pores with sizes ranging from 100 nm to 300 nm. At 37°C, BC-K_2CO_3 biochar was suitable for the time to equilibrium is 120 minutes, the optimal solid/liquid ratio was 0.5 g/mL, the input caffeine concentration less than 0.06 mg.mL^{-1}, the caffeine removal efficiency was 89.75 %. The caffeine adsorption of BC-K_2CO_3 biochar was consistent with Freundlich adsorption theory with high correlation coefficients R^2 (>0.992). Significantly, BC-K_2CO_3 exhibited a higher maximum adsorption capacity (Q_m = 33.74 mg.g^{-1}) compared to the control BC biochar (Q_m = 13.99 mg.g^{-1}), which was pyrolyzed without bioactive compound extraction. The effectiveness of BC-K_2CO_3 biochar as an efficient and environmentally friendly adsorbent for caffeine removal from water. The utilization of waste green coffee for biochar production offers a sustainable approach to address caffeine while adding value to the coffee industry's by-products.

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