

Removal of Formaldehyde from Aqueous Solution Using Low-cost and Reusable Adsorbents

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(Received 1 August 2022, Accepted 1 December 2022)

In this paper, activated carbon (AC) was utilized to eliminate formaldehyde from synthetic sewage. To this end, three kinds of activated carbon were used, which were commercial AC (CAC), AC derived from walnut shell (ACWS), and AC derived from lotus leaves (ACLL). Also, the influence of sorption time, formaldehyde concentration, and adsorbent dose on formaldehyde removal was investigated. The surface properties of the adsorbents were determined by SEM, FTIR and BET analyses. The results showed that CAC had higher specific surface area ($978.4 \text{ m}^2 \text{ g}^{-1}$) than the other adsorbents. The highest adsorption efficiency of formaldehyde using CAC, ACWS, and ACLL adsorbents was 99.2%, 88.2%, and 54%, respectively, indicating significant adsorption capacity of CAC compared to the other adsorbents. Also, the Langmuir isotherm model was fitted better to the laboratory data due to the higher R^2 value compared to the Freundlich model. Moreover, the experimental data followed the pseudo-second order kinetic model. The highest adsorption capacity of formaldehyde was 48.5 mg g^{-1} . Study of the reusability of adsorbents showed that the CAC had a remarkable recyclability and it could be used in seven cycles with high sorption efficiency (>90%).

Keywords: Activated carbon, Formaldehyde, Adsorption, Wastewater, Recyclability

INTRODUCTION

The rapid growth of industries in recent years has led to

the pollution of effluents [1]. These effluents enter the environment and cause various diseases for human and animals. Formaldehyde is one of the most toxic pollutants, which may be present in municipal and industrial effluents [2]. The vapor of formaldehyde has a pungent odor and

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irritates the skin and mucous membranes of the eyes, and has side effects such as respiratory disorders, asthma and carcinogenesis in the respiratory tract of animals and humans [2-3]. The US Environmental Protection Agency (EPA) also recognizes formaldehyde as a carcinogen. According to the EPA, the allowable limit of formaldehyde in drinking water must be 0.9 ppm [4]. Formaldehyde, with chemical formula of CH_2O , is generated in the effluent of glues, chemicals, petrochemicals and some parts of municipal wastewater. These industries produce formaldehyde with a concentration of more than 10 mg l^{-1} . Edward *et al.* classified 45 harmful chemicals and formaldehyde ranked first in the environmental impact ranking. 0.5% formaldehyde solution is able to kill microorganisms in a period of 6 to 12 h [5-7]. There are several methods for wastewater treatment such as membrane technology, filtration, ion-exchange, coagulation, demulsification, and adsorption process. Some of these methods are not suitable for treatment of wastewater containing formaldehyde. For example, biological treatment of formaldehyde is very complex and in many industries, formaldehyde-containing wastewater is collected in lagoons and evaporate over time, which causes formaldehyde to enter the air and contribute to the air pollution [8-10]. However, the adsorption process is a simple method with high adsorption capacity and high efficiency. Also, utilizing the adsorption process can not produce sludge [11].

Bioadsorbents are environmentally-friendly and cost-effective materials in the adsorption process. These adsorbents are synthesized by materials found in nature. Chitosan derived from shrimp waste can be used as a bioadsorbent [12]. During the adsorption process, the contaminants accumulate on the adsorbent surface and are separated from the solution. Adsorption takes place on the sorbent surface due to the attractive force between the functional groups on the sorbent surface and the solute molecules. So far, various sorbents have been utilized to treat sewage, among which, activated carbon (AC) is one of the most widely utilized. Due to its high specific surface area, AC has a significant adsorption capacity and can adsorb high amount of contaminants [13-14].

There are two steps for producing activated carbon, carbonization and activation. In the first step, activated carbon can be produced from carbonization of fruit's pit, tree's woods, tree's leaves, and so on (pyrolysis process). In

the second step, charcoal can be activated by chemicals such as NaOH. Pyrolysis of carbonaceous materials, without the presence of air, forms a carbonaceous solid. The produced material has a large number of cavities [13,15].

In this study, three types of activated carbon such as commercial AC (CAC), AC derived from walnut shell (ACWS), and AC derived from lotus leaves (ACLL) were utilized in removing formaldehyde from aquatic media. The structure of these adsorbents were determined by SEM, FTIR, and BET analyses. Also, effects of various variables such as time, temperature, adsorbent dosage and pH on formaldehyde adsorption were studied. Moreover, the thermodynamic, kinetic and equilibrium behaviors of the uptake of formaldehyde utilizing these sorbents were studied. In previous works, removing formaldehyde removal had been mostly performed by photocatalytic procedures, and its removal by CAC, ACWS, and ACLL sorbents has not been performed yet.

MATERIALS AND METHODS

Materials and Devices

Formaldehyde (COH_2) (Merck Company) was utilized to produce the stock solution. Digital scale (model: GR-200) was used to measure the weight of adsorbents. Moreover, commercial activated carbon was purchased from Sigma Aldrich Company (USA).

Synthesis of Lotus Leaves-derived Biochar and Walnut Shell Powder

Lotus leaves were used to synthesize biochar. To this end, at first, lotus leaves were washed by water for eliminating any dust and impurity. Then, they were heated at $80 \text{ }^\circ\text{C}$ for 50 min to evaporate water. Next, the dried leaves were calcined by the furnace at $800 \text{ }^\circ\text{C}$ for 3 h. After this step, lotus leaves-derived biochar was produced.

The second adsorbent was prepared by walnut shell. To do so, walnut shells were washed by distilled water to clean up their surface. Afterwards, they located in the oven at $80 \text{ }^\circ\text{C}$ for 50 min to dry. Next, walnut shells were located in a furnace at $800 \text{ }^\circ\text{C}$ for 3 h for calcination. Next, walnut shell powder as biochar was produced. Figure 1 displays images of these adsorbents.



Fig. 1. Images of the adsorbents used in this work.

After preparation of the adsorbents, SEM (JSM 6400, Japan), FTIR (Nicolet 6700, United States), and BET (2020ASAP, United States) analyses were used to characterize the adsorbents.

EXPERIMENTAL METHOD

In this study, the influence of several factors such as contact time, adsorbent concentration, and formaldehyde ion concentration was studied. Other factors such as pH, mixing rate, and temperature of solutions were considered 7, 100 rpm, and 25 °C, respectively. For this purpose, one variable was altered, while other variables were considered constant. First, the impact of time (10-200 min) on formaldehyde adsorption was surveyed. Next, a certain dose of adsorbent was added at room temperature to the solution with neutral pH. After each time, the solution was filtered and the sorbent was isolated. Then, the residual concentration of

formaldehyde in the solution was measured by Gas Chromatography (GC, VARIAN, model CP-3800GC).

After performing the tests, the uptake capacity (Q , mg g^{-1}) and uptake efficiency (AE, %) of formaldehyde were calculated through the Eqs. (1) and (2):

$$Q = \frac{(C_i - C_e)}{m} \times V \quad (1)$$

$$\text{AE}(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

Here, C_i , and C_e are the initial and equilibrium concentrations of formaldehyde (ppm), m is the sorbent weight (g), and V is the solution volume (l).

RESULTS AND DISCUSSION

Features of Sorbents

BET analysis can be utilized for measuring the surface attributes of materials including specific surface area, volume of pores, and mean pore diameter. In this study, the surface features of CAC, ACWS, and ACLL were determined by BET analysis and the outputs are given in Table 1. As it is clear, the active area of the adsorbents were very different. For example, the active area of CAC was $978.4 \text{ m}^2 \text{ g}^{-1}$, while this feature for ACWS and ACLL were 125.5 and $110.4 \text{ m}^2 \text{ g}^{-1}$, respectively. However, the pore diameter of the synthesized adsorbents were smaller than that of the commercial AC. The pore diameter of CAC, ACWS, and ACLL were 36.2, 22.1, and 12.1 nm, respectively, indicating that these three sorbents were mesoporous. Also, the pore volume for CAC, ACWS, and ACLL were determined as 0.487, 0.166, and $0.015 \text{ cm}^3 \text{ g}^{-1}$, respectively.

Table 1. BET Results for Three Adsorbents

Property	CAC	ACWS	ACLL
BET active area ($\text{m}^2 \text{ g}^{-1}$)	978.4	125.5	110.4
Diameter of pores (nm)	36.2	22.1	12.1
Density (g cm^{-3})	2.10	1.72	1.2
Ash (Wt.%)	38	15	20
Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	0.487	0.166	0.015

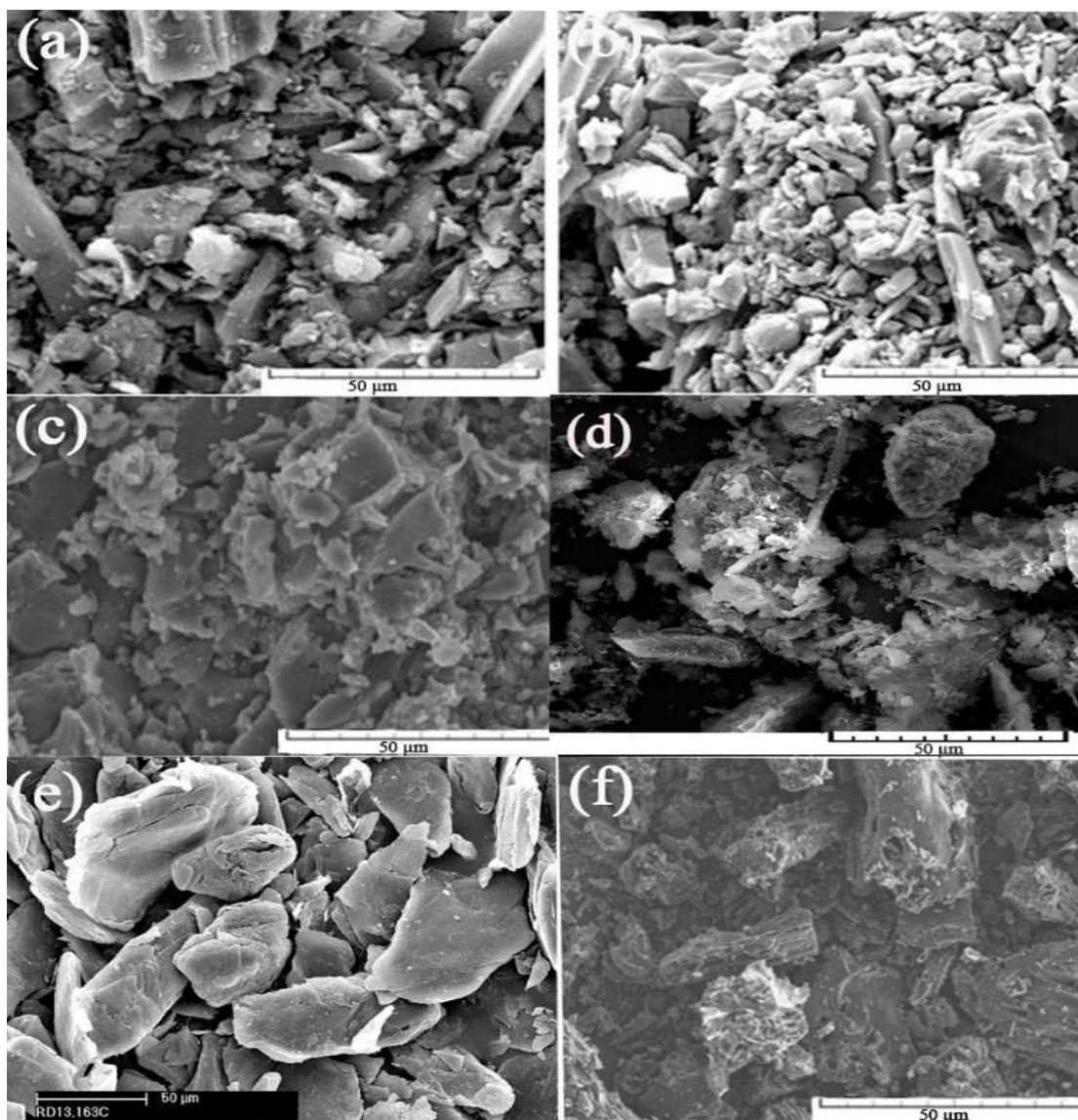


Fig. 2. SEM images of ACWS before (a) and after adsorption (b), ACLL before (c) and after adsorption (d) and CAC before (e) and after adsorption (f).

The morphology and surface change of adsorbents were identified by SEM analysis and the results of SEM for three types of AC before and after adsorption of formaldehyde are shown in Fig. 3. The greater the porosity and ups and downs on the adsorbent surface, the greater its specific surface area. Therefore, BET and SEM analyses are quite related. Before adsorption, there were many holes and pores on the sorbents surface, which were suitable for the uptake process. Also, many particles with different sizes were observed in the

structure of these adsorbents, which were connected to each other. These pores show that a large number of pollutant can be adsorbed by the adsorbent. By comparing these adsorbents, commercial AC had more active sites than other AC, indicating that it can be more suitable for adsorption. After adsorption, pores on the sorbent surface were covered by formaldehyde ions and significant changes were observed on the adsorbents' surface [16].

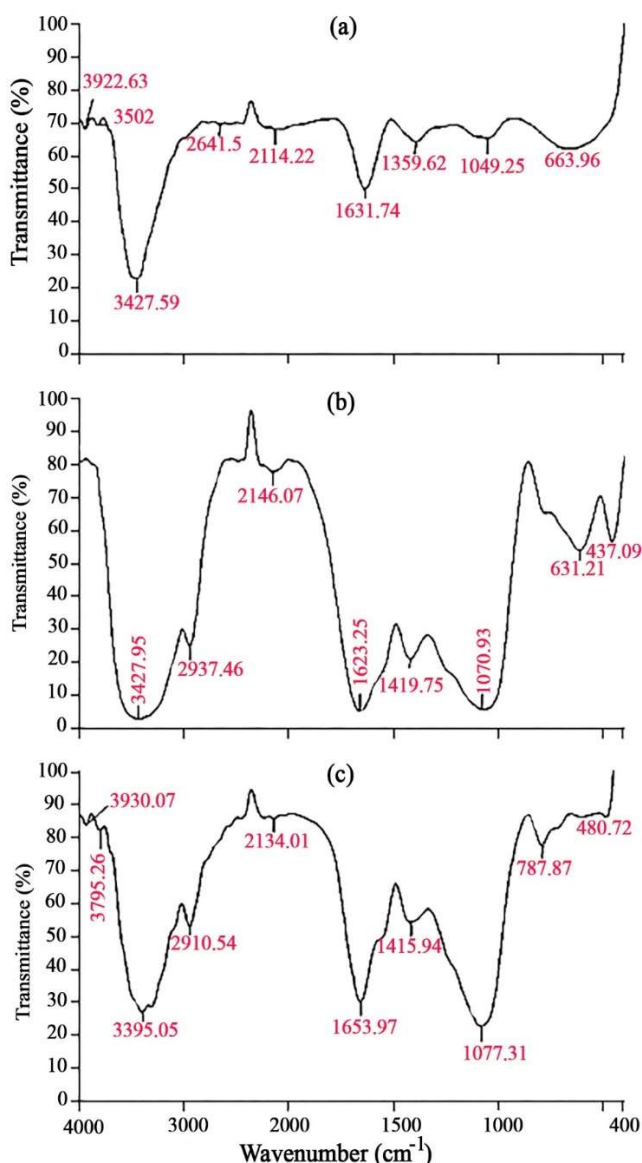


Fig. 3. FTIR analysis for ACWS (a), ACLL (b), and CAC (c) in the range of 400-4000 cm⁻¹.

Infrared spectroscopy is one of the most critical and extensively-employed procedures to identify molecular species. For identifying the functional groups on the sorbent surface, FTIR was used. The outcomes of FTIR spectra for the three adsorbents are shown in Fig. 3. In the structure of ACWS, two strong peaks were obtained at 3427.59 and 1631.74 cm⁻¹, attributing to the -OH and C=C functional groups. Also, several weak peaks were observed at 3502, 2370, 1359, 1049, and 663 cm⁻¹, relating to the -OH, -OH,

C-H, C-F, and N-H functional groups, respectively. Also, in the structure of ACLL, several peaks were obtained at 3427.95, 2937.46, 2146.07, 1623.25, 1419, 1070, 631, and 437 cm⁻¹, which were related to the -OH, =C-H, -OH, C=C, C-H, C-O, C-Br, and C-I, respectively. As shown, prominent peaks were observed in both adsorbents. In the structure of commercial AC, several peaks were also obtained at 3930, 3395, 2910, 2134, 1653, 1415, 1077, 787, and 480 cm⁻¹, which were related to the functional groups of N-H, -OH, -OH, -OH, C=C, C-H, C-O, C=C, and C-I, respectively [17-19]. The presence of these functional groups is very important in formaldehyde removal.

Adsorption Experiments

Contact time is an essential variable in the uptake process [20]. The impact of time on the formaldehyde adsorption capacity of three adsorbents (commercial AC, lotus leaves-derived AC, and walnut shell-derived AC) was studied in the range of 10-200 min, and the results are shown in Fig. 4. To this end, 0.5 g l⁻¹ of each adsorbent was separately added to the stock solution. Other parameters such as pH (7), formaldehyde concentration (10 ppm), and temperature (25 °C) were considered constant. As shown, the highest adsorption efficiency of formaldehyde using commercial AC, ACWS, and ACLL were 98.1%, 87.1%, and 46.6%, respectively, indicating that commercial AC had a higher adsorption efficiency than other adsorbents. The adsorption efficiency increased with an increment in contact time from 10 to 180 min, which can be due to more contact between adsorbate and adsorbent. Also, at early times, the number of active sites on the sorbent surface was more, resulting in an increase in the formaldehyde adsorption efficiency. After equilibrium time (180 min), no considerable change was obtained in the adsorption efficiency. Therefore, the optimum time was 180 min.

Adsorbent concentration is a key variable in the adsorption process as it specifies the adsorption capacity of a sorbent. Also, the amount of the sorbent affects the economy of the adsorption process [21]. The effect of sorbent concentration on the formaldehyde uptake process (0.2-1.2 g l⁻¹) was studied and the output is depicted in Fig. 5. The higher the amount of adsorbent is, the more active sites exist.

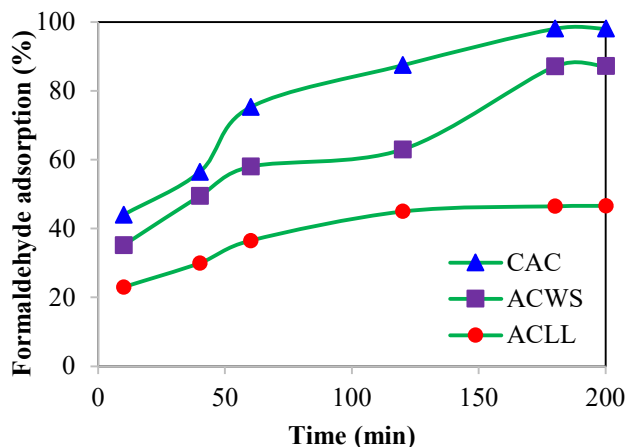


Fig. 4. Impact of time on the uptake of formaldehyde using CAC, ACWS, and ACLL.

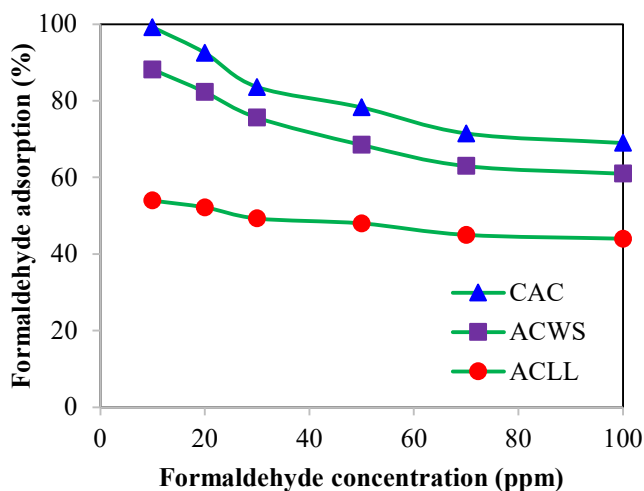


Fig. 6. Influence of formaldehyde concentration on uptake performance.

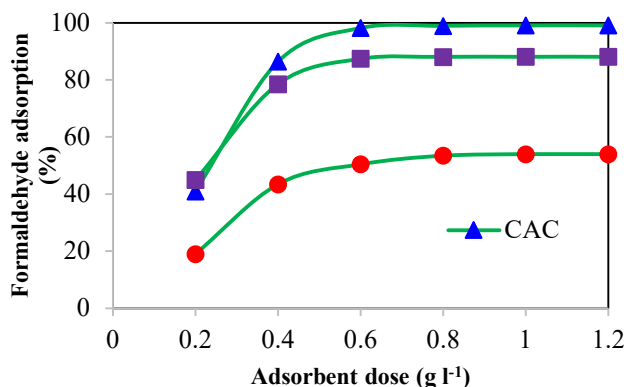


Fig. 5. Influence of adsorbent concentration on the adsorption process of formaldehyde utilizing CAC (a), ACWS (b), and ACLL (c).

As indicated, the adsorption efficiency of formaldehyde increases with an increase in the amount of adsorbent; this is because the number of active sites on the sorbent surface increases and more formaldehyde ions can be adsorbed on the sorbent surface. As the sorbent concentration increased from 0.2 to 1 g l⁻¹ the uptake efficiency increased from 41 to 99.2% for commercial AC, 45 to 88.2% for walnut shell AC, and 19% to 54% for ACLL. At above 1 g l⁻¹ adsorbent dosage, no change was observed in the formaldehyde uptake efficiency. Therefore, the sorbent concentration of 1 g l⁻¹ was considered as the optimum amount for all adsorbents.

Moreover, the concentration of formaldehyde has a critical role on the uptake process; thus, the impact of this parameter in the range of 10-100 ppm was studied. Figure 6 indicates the impact of formaldehyde concentration on adsorption. Other factors such as pH of 7, temperature of 25 °C and sorbent dose of 1 g l⁻¹ were kept constant. As shown, the uptake of formaldehyde decreased with an increase in formaldehyde concentration and the maximum adsorption efficiency occurred at 10 ppm. At low formaldehyde concentrations, the number of active sites on the adsorbent surface is greater than the number of pollutant molecules, which causes more adsorption. With an increase in the formaldehyde concentration, there are fewer active sites for all pollutants; this decreases the adsorption efficiency. Therefore, the optimum concentration of formaldehyde was 10 ppm and at this concentration, the uptake efficiency of formaldehyde using CAC, ACWS, and ACLL was 99.2, 88.2, and 54%, respectively.

Equilibrium Investigation of Formaldehyde Adsorption

Sorption isotherms can determine the relationship between the sorption capacity and adsorbate concentration. They can specify the utmost uptake capacity of a sorbent and its nature (physical or chemical). Also, adsorption isotherms are very important to describe the interaction between

adsorbent and adsorbate. The adsorption of contaminants in the first layer is influenced by the interaction between the adsorbent and adsorbate. In the other layers, the highest pollutant adsorption is due to the adsorbate-adsorbate interaction and the lowest adsorption is because of the adsorbate-sorbent interaction. Due to the small size of the formaldehyde molecule, there is a smaller adsorbate-adsorbent interaction force and a larger adsorbate-adsorbate interaction force between them [22-23]. In this study, the Langmuir and Freundlich models were used to study the equilibrium behavior of the formaldehyde adsorption process using commercial AC. In the Langmuir isotherm equation, it is assumed that the adsorption occurs on the homogeneous surface of the adsorbent and the adsorption process contains single layer. In the Freundlich model, the sorption process occurs on the heterogeneous surface of the sorbent. Equation (3) and Eq. (4) give the Langmuir and Freundlich equations, respectively [24-25]:

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

$$q_e = K_f C_e^{1/n} \quad (4)$$

Here, C_e , q_e , q_{max} , K_L , and K_F are the equilibrium concentration of formaldehyde (ppm), the uptake capacity at equilibrium (mg g^{-1}), the utmost uptake capacity (mg g^{-1}), the Langmuir constant (l mg^{-1}), and the Freundlich constant ($(\text{mg g}^{-1})(\text{mg l}^{-1})^{-1/n}$), respectively. Also, n is the homogeneity factor and determines whether the uptake process is desirable (physical) or undesirable (chemical). If $n > 1$, the uptake process is favorable and *vice versa* [25-26]. Also, K_L depends on temperature and is attributed to the bond strength between the adsorbate and the adsorbent. In this study, a solution with a formaldehyde concentration of

5 ppm was prepared and 1 g l^{-1} of adsorbent was added to it. After 180 min, the adsorption process was stopped and the residual concentration of formaldehyde in the solution was specified. The results of isothermal behavior for adsorption of formaldehyde using commercial AC are shown in Fig. 7 and the data extracted are reported in Table 2.

The correlation coefficient (R^2) for the Freundlich and Langmuir models were 0.91 and 0.96, respectively, indicating a larger R^2 for the Langmuir model compared to the Freundlich model. By comparing the R^2 value for the two models, it is concluded that the uptake of formaldehyde by the commercial AC follows the Langmuir model. Therefore, a single layer of formaldehyde is adsorbed on the adsorbent surface. Also, the maximum adsorption capacity of formaldehyde by the Langmuir model was 48.5 mg g^{-1} , which is a suitable amount. Moreover, the amount of n is 9.1 (>1), indicating that the adsorption process of formaldehyde by the commercial AC is favorable. Furthermore, the root mean square error (RMSE) was utilized for determining the

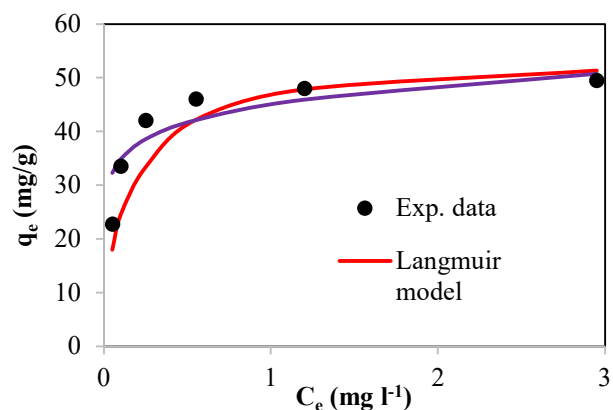


Fig. 7. Equilibrium investigation of the formaldehyde uptake process using the Langmuir (a) and Freundlich (b) non-linear models.

Table 2. Equilibrium Parameters of the Formaldehyde Adsorption Process

Langmuir				Freundlich			
R^2	RMSE	q_{max} (mg g^{-1})	K_L (l mg^{-1})	R^2	RMSE	K_F (mg g^{-1})	n
0.96	0.92	48.5	6.5	0.91	2.58	45.4	9.1

relationship between the predicted values by the two models and the experimental data. The smaller the RMSE, the better the model can fit the data [27-28]. As shown in Table 2, the RMSE values for the Freundlich and Langmuir models were 2.58 and 0.92, respectively, indicating that the Langmuir model could better predict the equilibrium behavior.

Our results were compared with previous studies that are reported in Table 3. As shown, the sorption efficiency of CAC is higher than the other sorbents presented in Table 3. Also, compared to other adsorbents, the adsorption capacity of CAC is more significant (48.5 mg g⁻¹).

Adsorption Kinetics

Kinetic study shows the removal rate of formaldehyde from a solution. Also, it controls the resistance of the contaminant at the interface of solid-liquid. In the primary step of the adsorption process, the removal rate of ions was higher, which might be due to the presence of empty active sites on the activated carbon surface. Adsorption kinetics is also dependent on the active area of the sorbent as well as active sites of the sorbent that are suitable for trapping formaldehyde ions [29]. For determining the removal mechanism of formaldehyde using the commercial AC, the quasi-first order (QFO, Eq. (5)) and quasi-second order (QSO, Eq. (6)) models were used [30]:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (5)$$

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

Here, k_1 (1 min⁻¹), q_t (mg g⁻¹), q_e (mg g⁻¹), and k_2 (g mg⁻¹ min⁻¹) are the QFO kinetic constant, the uptake capacity of formaldehyde at t , the uptake capacity at equilibrium time, and the QSO kinetic constant, respectively [31-32]. In the QFO model, a strong adsorbent-adsorbate interaction is assumed to be the rate-controlling step. The QSO model can be used to describe the penetration of solids that is not correctly defined by the QFO model [33]. The results of kinetic study of the adsorption process are displayed in Fig. 8 (a and b) and Table 4. According to R² values, the QSO model could better describe the kinetic investigation of the formaldehyde adsorption process by the commercial AC than the QFO model. The amount of $q_{e,cal}$ for QFO (5.88 mg g⁻¹) was greater than that of QSO (5.2 mg g⁻¹). Also, the kinetic constants of K_1 and K_2 were 0.015 min⁻¹ and 0.0125 g mg⁻¹ min⁻¹, respectively. Moreover, the value of RMSE for QFO and QSO models was 0.73 and 0.45, respectively, indicating that the QSO equation could better predict the kinetic behavior of the uptake process. Therefore, the adsorption of formaldehyde using the

Table 3. Comparison of the Adsorption Capacity and Adsorption Efficiency of the Sorbents Used in This Work with other Adsorbents for Formaldehyde Removal

Adsorbent	Adsorption capacity (mg g ⁻¹)	Adsorption efficiency (%)	Ref.
Ground kaolin	3.41	80	[2]
bentonite	5.03	90	[2]
Zeolite	0.393	82	[5]
Zeolite modified by H ₂ SO ₄	0.429	95	[5]
AC	19.86	94.73	[7]
AC/Fe ₃ O ₄	24.21	95.67	[7]
CaO/Fe ₃ O ₄	21.28	95.14	[7]
AC/Fe ₃ O ₄ /CaO	24.01	98.22	[7]
Activated carbon fiber	14.34	-	[11]
CAC	48.5	99.2	Present study
ACWS	-	88.2	Present study
ACLL	-	54	Present study

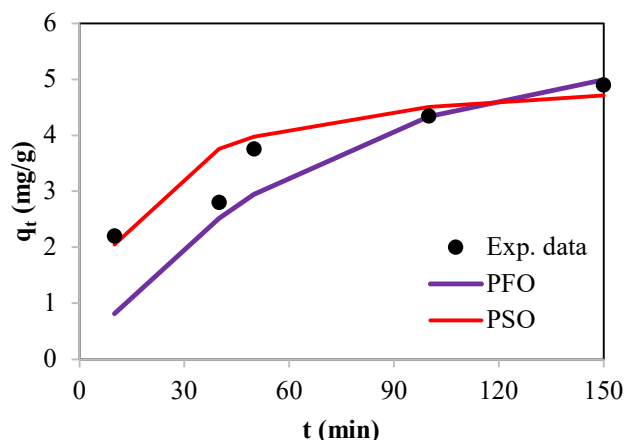


Fig. 8. Adsorption kinetics of formaldehyde by commercial AC, including QFO (a) and QSO (b) kinetic equations.

Table 4. Parameters of Kinetic Study of the Formaldehyde Uptake Process Utilizing Commercial AC

Model	Parameter	Value
QFO	R^2	0.944
	RMSE	0.73
	$q_{e,cal}$ (mg g^{-1})	5.88
	K_1 (min^{-1})	0.015
QSO	R^2	0.958
	RMSE	0.45
	$q_{e,cal}$ (mg g^{-1})	5.2
	K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.0125

commercial AC follows the QSO kinetic. Fitting the empirical data with the QSO model indicated that the interaction between the adsorbate molecules and the adsorbent was chemical [33-34].

Recyclability of Adsorbents

One of the most critical variables on the economic feasibility of adsorbents is their recyclability in the adsorption process [35]. To this end, this feature was investigated for three adsorbents in the eliminating formaldehyde from effluents. After using the adsorbent in the uptake process, the sorbent was separated from the solution and washed by HCl solution to remove any formaldehyde

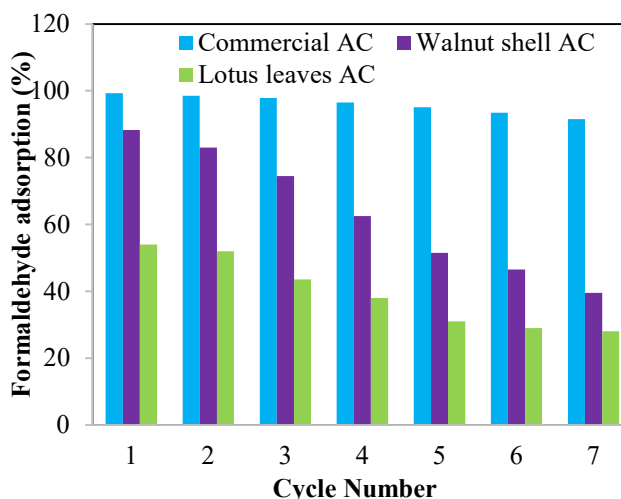


Fig. 9. Recyclability of CAC, ACWS, and ACLL in removing formaldehyde from aqueous solutions in 7 reuse cycles.

from its surface and then reused in the adsorption of formaldehyde. This process was done in 7 reuse cycles and after each step, the adsorption efficiency of formaldehyde by the adsorbents was calculated. Figure 9 shows the reusability of adsorbents. All experiments were performed in optimal conditions (sorbent concentration of 1 g l^{-1} , time of 150 min for commercial AC and 180 for lotus leaves-derived AC and walnut shell-derived AC adsorbents, neutral pH, $25 \text{ }^\circ\text{C}$, mixing rate of 100 rpm, and formaldehyde concentration of 5 ppm). As shown, commercial AC showed the highest recyclability among these three adsorbents, so that after the seventh cycle, its adsorption efficiency reduced from 99.2% to 91.5%, which is a significant removal efficiency. However, the adsorption efficiency of formaldehyde by the ACWS reduced from 88.2% to 39.5%, indicating that the adsorption efficiency was decreased significantly. The same results was attained by ACLL and the adsorption efficiency of formaldehyde reduced from 54% to 28%. Therefore, commercial AC had a higher recyclability than ACWS and ACLL for formaldehyde removal and it is more economical in the adsorption process. Wang *et al.* (2022) studied the reusability of a 13X molecular sieve in six cycles and found that after the sixth cycle, the removal efficiency was 92% of the first step, while the removal efficiency of commercial AC in this work after the sixth cycle was 93.4%, which is higher

than 13X molecular sieve [36]. In another study, Salman *et al.* (2011) investigated the reusability of date seed activated carbon. After three steps, the removal efficiency of bentazon and carbofuran was 84.1 and 82.2%, respectively, which had less reusability than our study [37].

CONCLUSIONS

Formaldehyde content higher than the standard value of 1 mg l^{-1} in effluent has negative effects on the environment. Here, the removal of formaldehyde from the effluent was investigated using different adsorbents. For doing so, the influence of various variables such as adsorbent type (commercial activated carbon, walnut shell-derived activated carbon, and lotus leaves-derived activated carbon), contact time (10-240 min), formaldehyde concentration (10-100 ppm), and adsorbent concentration ($0.2\text{-}1.2 \text{ g l}^{-1}$) on the formaldehyde sorption rate was investigated. According to the results, the highest adsorption efficiency by the commercial activated carbon, walnut shell-derived activated carbon, and lotus leaves-derived activated carbon was 99.2%, 88.2%, and 54%, respectively, indicating on higher adsorption efficiency for commercial AC compared to the other two adsorbents. Also, the equilibrium behaviour of the formaldehyde uptake process using commercial AC indicated that the Langmuir equation can better describe the isothermal behaviour of the adsorption process and the utmost sorption capacity by this model was attained as 48.5 mg g^{-1} . Moreover, the Freundlich model showed that the adsorption of formaldehyde by the adsorbent is favourable and physical. In addition, the kinetic study showed that the empirical data were fitted to the QSO kinetic equation due to a larger R^2 . Furthermore, the adsorption efficiency of the commercial AC reduced from 99.2 to 91.5% after 7 reuse cycles, indicating high recyclability of this sorbent. Generally, the recyclability of these three adsorbents showed that commercial AC had a higher recyclability than walnut shell-derived AC and lotus leaves-derived AC for formaldehyde removal and it is more economical for being used in the adsorption process.

REFERENCES

- [1] Jasim, L. S.; Aljeboree, A. M., Hydrogels in the removal of industrial pollution: Adsorption characteristics for the removal of a toxic dye from aqueous solutions. *Casp. J. Environ. Sci.* **2021**, *19*, 789-799. <https://doi.org/10.22124/cjes.2021.5209>.
- [2] Salman, M.; Athar, M.; Shafique, U.; Rehman, R., Removal of formaldehyde from aqueous solution by adsorption on kaolin and bentonite: a comparative study. *Turkish J. Eng. Environ. Sci.* **2012**, *36*, 263-270. <https://doi.org/10.3906/muh-1109-8>.
- [3] Bednarik, V.; Vondruska, M., Removal of Formaldehyde from Acrylic Acid Production Wastewater. *Environ. Eng. Sci.* **2003**, *20*, 703-707. <https://doi.org/10.1089/109287503770736203>.
- [4] Nájera-Estebanjuan, G.; Carrillo-Cedillo, E. G.; Cañizares-Macías, M. P., Development and validation of a novel fluorescence method via sequential injection analysis to determine formaldehyde in drinking water. *Anal. Methods* **2019**, *11*, 2041-2049. <https://doi.org/10.1039/C9AY00228F>.
- [5] Paliulis, D., Removal of Formaldehyde from Synthetic Wastewater Using Natural and Modified Zeolites. *Pol. J. Environ. Stud.* **2016**, *25*, 251-257. <https://doi.org/10.15244/pjoes/60727>.
- [6] Takano, T.; Murakami, T.; Kamitakahara, H.; Nakatsubo, F., Formaldehyde adsorption by karamatsu (*Larix leptolepis*) bark. *J. Wood Sci.* **2008**, *54*, 332-336. <https://doi.org/10.1007/s10086-007-0940-6>.
- [7] Khaleghi, H.; Esmaceli, H.; Jaafarzadeh, N.; Ramavandi, B., Date seed activated carbon decorated with CaO and Fe_3O_4 nanoparticles as a reusable sorbent for removal of formaldehyde. *Korean J. Chem. Eng.* **2022**, *39*, 146-160. <https://doi.org/10.1007/s11814-021-0972-4>.
- [8] Akinterinwa, A.; Oladele, E.; Adebayo, A.; Ajayi, O., Synthesis of Cross-Linked Carboxymethyl Legume Starch for Adsorption of Selected Heavy Metals from Aqueous Solutions. *Adv. J. Chem. A.* **2020**, *3*, 594-611. <https://doi.org/10.22034/ajca.2020.105801>.
- [9] Amar, I.; Sharif, A.; Ali, M.; Alshareef, S.; Altohami, F.; Abdulqadir, M.; Ahwidi, M., Removal of methylene blue from aqueous solutions using nano-magnetic adsorbent based on zinc-doped cobalt ferrite. *Chem. Methodol.* **2020**, *4*, 1-18. <https://doi.org/10.33945/sami/chemm.2020.1.1>.
- [10] Etim, U. J.; Zhong, Z.; Yan, Z.; Bai, P., 3. Functional

- catalysts for catalytic removal of formaldehyde from air. *Environmental Functional Nanomaterials*. De Gruyter 2020, **2019**, 89-126. <https://doi.org/10.1515/9783110544183-003>.
- [11] Song, Y.; Qiao, W.; Yoon, S.; Mochida, I.; Guo, Q.; Liu, L., Removal of formaldehyde at low concentration using various activated carbon fiber. *J. Appl. Polym. Sci.* **2007**, *106*, 2151-2157. <https://doi.org/10.1002/app.26368>.
- [12] Gerhardt, R.; Farias, B. S.; Moura, J. M.; de Almeida, L. S.; da Silva, A. R.; Dias, D.; Cadaval Jr, T. R.; Pinto, L. A., Development of chitosan/Spirulina sp. blend films as biosorbents for Cr⁶⁺ and Pb²⁺ removal. *Int. J. Biol. Macromol.* **2020**, *155*, 142-152. DOI: <https://doi.org/10.1016/j.ijbiomac.2020.03.201>.
- [13] Rafiee, P., Determination of heavy metal pollution products, vegetable gardens Ardabil. *Journal of Research in Science, Engineering and Technology* **2018**, *6*, 6-13. <https://doi.org/10.24200/jrset.vol6iss04pp6-13>.
- [14] Fagbohun, E. O.; Wang, Q.; Spessato, L.; Zheng, Y.; Li, W.; Olatoye, A. G.; Cui, Y., Physicochemical regeneration of industrial spent activated carbons using a green activating agent and their adsorption for methyl orange. *Surf. Interfaces* **2022**, *29*, 101696. <https://doi.org/10.1016/j.surf.2021.101696>.
- [15] Afdhol, M. K.; Amiliana, R. A.; Hanafi, A.; Rachmanda, B., March. Preparation of activated carbon from palm shells using KOH and ZnCl₂ as the activating agent. *IOP Conf. Ser. Mater. Sci. Eng.* **2017**, *180*, 012282. <https://doi.org/10.1088/1755-1315/75/1/012009>.
- [16] Ameri Akhtiar Abadi, M.; Masrounia, M.; Abedi, M. R., Simultaneous Extraction and Preconcentration of Benzene, Toluene, Ethylbenzene and Xylenes from Aqueous Solutions Using Magnetite–Graphene Oxide Composites. *Chem. Methodol.* **2021**, *5*, 11-20. <https://doi.org/10.22034/chemm.2021.118260>.
- [17] Takmil, F.; Esmaeili, H.; Mousavi, S. M.; Hashemi, S. A., Nano-magnetically modified activated carbon prepared by oak shell for treatment of wastewater containing fluoride ion. *Adv. Powder Technol.* **2020**, *31*, 3236-3245. <https://doi.org/10.1016/j.apt.2020.06.015>.
- [18] Zhang, L.; Tu, L. Y.; Liang, Y.; Chen, Q.; Li, Z. S.; Li, C. H.; Wang, Z. H.; Li, W., Coconut-based activated carbon fibers for efficient adsorption of various organic dyes. *RSC Adv.* **2018**, *8*, 42280-42291. <https://doi.org/10.1039/C8RA08990F>.
- [19] Sulaymon, A. H.; Abood, W. M., Removal of reactive yellow dye by adsorption onto activated carbon using simulated wastewater. *Desalin. Water Treat.* **2014**, *52*, 3421-3431. <https://doi.org/10.1080/19443994.2013.800341>.
- [20] Jasim, L. S.; Aljeboree, A. M., Hydrogels in the removal of industrial pollution: Adsorption characteristics for the removal of a toxic dye from aqueous solutions. *Casp. J. Environ. Sci.* **2021**, *19*, 789-799. <https://doi.org/10.22124/cjes.2021.5209>.
- [21] Gopal, K.; Mohd, N. I.; Raoov, M.; Suah, F. B. M.; Yahaya, N.; Zain, N. N. M., Development of a new efficient and economical magnetic sorbent silicone surfactant-based activated carbon for the removal of chloro- and nitro-group phenolic compounds from contaminated water samples. *RSC Adv.* **2019**, *9*, 36915-36930. <https://doi.org/10.1039/C9RA07151B>.
- [22] Zhu, L.; You, L.; Wang, Y.; Shi, Z., The application of graphitic carbon nitride for the adsorption of Pb²⁺ ion from aqueous solution. *Mater. Res. Express* **2017**, *4*, 075606. <https://doi.org/10.1088/2053-1591/aa7903>.
- [23] Saleh Ibrahim, A.; Chyad Al-Hamadani, R. F.; Fahim Chyad, T.; H Ali, S., Using ozone for activation of manufactured porous media to improve the removal efficiency of heavy metals from industrial wastewater. *Casp. J. Environ. Sci.* **2022**, *20*, 283-294. <https://doi.org/10.22124/cjes.2022.5559>.
- [24] Marques Jr, J. L.; Lütke, S. F.; Frantz, T. S.; Espinelli Jr, J. B. S.; Carapelli, R.; Pinto L. A. A.; Cadaval Jr, T. R. S., Removal of Al(III) and Fe(III) from binary system and industrial effluent using chitosan films. *Int. J. Biol. Macromol.* **2018**, *120*, 1667-1673. <https://doi.org/10.1016/j.ijbiomac.2018.09.135>.
- [25] Kzar, H. H.; Salahdin, O. D.; Arenas, L. A. B.; Parra, R. M. R.; Aravindhan, S.; Mohammed, F.; Ansari, M. J.; Al-Gazally, M. E.; Uktamov, K. F.; Hamza, T. A.; Aldulaim, A. K. O., Solamen Vaillant Mollusk Powder as an Efficient Biosorbent for Removing Cobalt Ions from Aqueous Solution: Kinetic and Equilibrium Studies. *Phys. Chem. Res.* **2023**, *11*, 159-169. <https://doi.org/10.22036/PCR.2022.336422.2073>.

- [26] da Rosa, M. P.; Igansi, A. V.; Lütke, S. F.; Junior, T. R. S. A. C.; do Santos, A. C. R.; Inacio, A. P. D. O. L.; de Almeida Pinto, L. A.; Beck, P. H., A new approach to convert rice husk waste in a quick and efficient adsorbent to remove cationic dye from water. *J. Environ. Chem. Eng.* **2019**, *7*, 103504. <https://doi.org/10.1016/j.jece.2019.103504>.
- [27] Rusanov, A. I.; Dmitrieva, O. A.; Mamardashvili, N. Z.; Tetko, I. V., More Is Not Always Better: Local Models Provide Accurate Predictions of Spectral Properties of Porphyrins. *Int. J. Mol. Sci.* **2022**, *23*, 1201. <https://doi.org/10.3390/ijms23031201>.
- [28] Alshamri, A. M. J.; Aljeboree, A. M.; Alqaragully, M. B.; Alkaim, A. F., Removal of toxic textile dyes from aqueous solution through adsorption onto coconut husk waste: Thermodynamic and isotherm studies. *Casp. J. Environ. Sci.* **2021**, *19*, 513-522. <https://doi.org/10.22124/cjes.2021.4937>.
- [29] Vaddi, D.; Lakshmi Prasad, M., Bio-sorption of As(V) from Aqueous Solutions by Thuja Occidentalis Leaves Activated Carbon@ Al Embedded Material. *Phys. Chem. Res.* **2023**, *11*, 287-297. <https://doi.org/10.22036/PCR.2022.335166.2064>.
- [30] Dogar, S.; Nayab, S.; Farooq, M. Q.; Said, A.; Kamran, R.; Duran, H.; Yameen, B., Utilization of biomass fly ash for improving quality of organic dye-contaminated water. *ACS Omega* **2020**, *5*, 15850-15864. <https://doi.org/10.1021/acsomega.0c00889>.
- [31] Alwan Al Mashhadani, A. M.; Himdan, T. A.; Hamadi Al Dulaimi, A. S.; AbuZaid, Y. I. M., Adsorptive removal of some carbonyl containing compounds from aqueous solutions using Iraqi porcelanite rocks: a kinetic-model study. *Casp. J. Environ. Sci.* **2022**, *20*, 117-129. <https://doi.org/10.22124/cjes.2022.5406>.
- [32] Esmaceli, H.; Tamjidi, S., Ultrasonic-assisted synthesis of natural clay/Fe₃O₄/graphene oxide for enhance removal of Cr(VI) from aqueous media. *Environ. Sci. Pollut. Res.* **2020**, *27*, 31652-31664. <https://doi.org/10.1007/s11356-020-09448-y>.
- [33] Álvarez-Gutiérrez, N.; Gil, M. V.; Rubiera, F.; Pevida, C., Kinetics of CO₂ adsorption on cherry stone-based carbons in CO₂/CH₄ separations. *Chem. Eng. J.* **2017**, *307*, 249-257. <https://doi.org/10.1016/j.cej.2016.08.077>.
- [34] Mostofi, F., Heavy metal contamination of zinc and lead in Region 1 and 2 of the main city of Ardabil. *Journal of Research in Science, Engineering and Technology*, **2018**, *6*, 14-20. <https://doi.org/10.24200/jrset.vol6iss04pp14-20>.
- [35] Bayuo, J.; Abukari, M. A.; Pelig-Ba, K. B., Desorption of chromium(VI) and lead(II) ions and regeneration of the exhausted adsorbent. *Appl. Water Sci.* **2020**, *10*, 171. <https://doi.org/10.1007/s13201-020-01250-y>.
- [36] Wang, S.; Wang, Y.; Kuang, Y.; Xu, S.; Gao, S.; Liu, L.; Niu, H.; Xiao, P.; Huang, B., Adsorption behaviour of molecular sieve and activated carbon for CO₂ adsorption at cold temperatures. *Carb. Neutrality* **2022**, *1*, 1-9. <https://doi.org/10.1007/s43979-022-00017-5>.
- [37] Salman, J. M.; Njoku, V. O.; Hameed, B. H., Bentazon and carbofuran adsorption onto date seed activated carbon: kinetics and equilibrium. *Chem. Eng. J.* **2011**, *173*, 361-368. <https://doi.org/10.1016/j.cej.2011.07.066>.