Annals of Biology **39** (1) : 41-48, 2023

Impact Score : 0.32 (Scopus)

Preparation, Characterization and Assessment of Low Cost Green Adsorbent Prepared from Coconut Shell for Removal of Toxic Dichloromethane

ANJU MANGOTRA*, SHAILESH KUMAR SINGH[1] AND ANAND MOHAN

School of Bioengineering and Biosciences, Lovely Professional University, Phagwara-144 411 (Punjab), India
**(e-mail: anju20004@gmail.com; Mobile: 89686 73268)*

(Received: June 20, 2022; Accepted: July 21, 2022)

ABSTRACT

The seamless release of industrial effluents and deterioration of the physico-chemical properties of water are becoming a prolonged threat across the world. Industrial effluents including dichloromethane have deleterious effects on the water chemistry and make the zooplankton difficult to breathe and furthermore affect the metabolism of aerobic aquatic species. The aim of this study was to prepare low-cost porous coconut shell activated carbon (CSAC) and further analyze and investigate its capability to adsorb dichloromethane. The carbonization process was carried out at a temperature of 700°C. The activation of carbon was brought into forth by using phosphoric acid (H_3PO_4) as activating agent. Impregnation ratio was taken as 1 : 3 and the activation time was kept 1 h. The characterization of the resulting porous carbon was accomplished using sophisticated Fourier transform infrared spectroscopy and well-refined field emission electron microscopy. Adsorption capacities and removal percentages of samples were investigated by batch studies. Langmuir and Freundlich adsorption isotherms were used for the evaluation of adsorption process. The experimental data were best fitted in the Freundlich model. Various parameters such as thermodynamics, kinetics, pH and concentration of adsorbate, dosages of adsorbent and contact time on dichloromethane adsorption were investigated. The removal of dichloromethane by CSAC was evaluated to be 87.5%. The results of this study divulged that activated carbon produced from coconut shell by chemical activation was a justifiable adsorbent for treatment of volatile organic compounds in wastewaters.

Key words: Activated carbon, coconut shell, volatile compounds, chemical activation, isotherm models

INTRODUCTION

Industrial effluents entail the volatile organic compounds discharged into the water bodies and drastically alter the water chemistry (Asejeje *et al.,* 2021; Gang *et al.,* 2021; Hernández-Fernández *et al.,* 2021). It became a prime concern for the researchers to work on the evacuation of these malodorous compounds from the watercourse. Adsorption by carbon has seized substantial attention in the past decades due to its positive attributes of high surface area, easy availability, hydrophobicity, tremendous pore volume distribution, extensive pore size distribution, removal effectiveness at less concentration, reutilizing ability, low energy consumption and probability of product repossession. These are gaining momentum in the purification of organic compounds due to having property of extreme porosity and high efficacy of surface reactivity (Li *et al.,* 2020 a, b; 2021). In terms of cost, financial compatibility, sustainability, efficiency and eco-friendly nature, activated carbon is the most preferred choice (Lv *et al.,* 2019; Singh *et al.,* 2019; Wen *et al.,* 2019). This is a porous material having delineating amphoteric properties, and is conventionally utilized for adsorption of organic and inorganic compounds (Heidarinejad *et al.,* 2020; Zhu *et al.,* 2020; Li *et al.,* 2021). Among many adsorbents of agricultural origin, activated carbon prepared from coconut shell is attempted and acknowledged material with good adsorption capacity in the removal of volatile organic compounds present in the sample matrix. It has given the best results in the removal of compounds such as chloroform, carbon disulphide, acetone, phenol, methyl isoborneol, geosmin, toluene, chlorobenzene, xylene, benzene, methyl ter-butyl ether, trichloroethylene, trichloroacetic acid and mesitylene from the sample matrix (Hao *et al.,* 2018; Zhao *et al.,* 2018). In the

[1]School of Agriculture, Lovely Professional University, Phagwara-144 411 (Punjab), India.

preparation of activated carbon from biomass, carbonization and activation are the prime steps (Lam *et al.,* 2017; Nayak *et al.,* 2017). The activation process is categorized into physical and chemical activation. Chemical activation is an ideal choice due to low temperature, short activation time, low activation temperature, better porous structure, and huge carbon content and high surface area yield. Physical activation involves carbonization of a carbonaceous material followed by the activation at elevated temperature with appropriate oxidizing gases with environmentally friendly attribute (Udyani and Purwaningsih, 2021). The aim of the present study was to prepare and characterize the activated carbon made from coconut shell at a laboratory level and its further use in investigation of its potential as a good adsorbent for removal of the malodorous organic compound-dichloromethane.

MATERIALS AND METHODS

Coconut shell was collected from the local market. It was washed intensively with deionized water to detach the dirt particles and sun-dried for 3-4 days. Subsequently, it was dried by keeping it in an oven at 105°C for 48 h and thereafter, milling was done. The milled precursor was screened to the desired size to prepare the adsorbent (Liang *et al.*, 2020; Yagmur and Kaya, 2021). Carbonization and activation were carried out as per the previous studies (Basu *et al.*, 2018).

For the analysis of physio-chemical properties of adsorbent standard methods were applied (Jian *et al.*, 2018). The characterization of the resulting porous carbon was executed using Fourier transform infrared spectroscopy and field emission electron microscopy (Soleimanpour *et al.*, 2021; Ismail *et al.*, 2022). The stock solution of dichloromethane (DCM) was prepared by applying standard methods (Cen *et al.*, 2018; Alhooshani, 2019). Analytical grade chemicals and reagents were used. The physical properties of DCM are shown in Table 1. The concentrations of dichloromethane in samples are detected by using UV-visible spectrophotometer until the equilibrium was reached (normally after 4 h; Li *et al.*, 2020a; Zhang *et al.*, 2020b). For the adsorption studies, desired concentration of adsorbate solution was equilibrated with known adsorbent dosage

Table 1. Physical properties of dichloromethane

Particulars	Unit	Dichloromethane
Formula		CH_2Cl_2
Molecular weight MW	g/mol	84.93
Normal boiling point	°C	39.8
Liquid density at 20°C	g/cm^3	1.318
Solubility in water	Mass%	1.32
Vapor pressure at 293 K	mm Hg	350

in 50 ml glass flasks in a temperature controlled water bath shaker for 4 h at 150 rpm. The samples were analyzed, and adsorption capacity and removal efficiency were calculated following Li *et al.* (2020a) and Zhang *et al.* (2020b). Various parameters such as effect of pH, initial concentration of adsorbate, adsorbent doses and contact time were studied by taking adsorbate solution (25 ml) with initial concentration of 200 mg/l into 50 ml capped glass flasks.

In order to study the various parameters, all the other parameters were kept constant except the parameter to be analyzed. The effect of pH on adsorption was studied by bringing variation in the pH value and keeping other parameters constant (Mahmoud *et al.*, 2021). To investigate the effect of contact time on adsorption, the other parameters such as adsorbent dosage (0.1 g), pH (7), initial concentration of adsorbate (200 mg/l), agitation time (150 rpm) and temperature 25°C were kept constant except contact time (1-240 min; Mahmoud *et al.*, 2021). The impact of adsorbent dosages on adsorption of dichloromethane was studied by taking variation in adsorbent dosages from 0.2-1.0 g keeping other parameters as constant (Mahmoud *et al.*, 2021). The effect of initial DCM concentration on the adsorption was investigated by taking variations in the concentration of adsorbate (DCM) keeping other factors constant (Mahmoud *et al.*, 2021). Langmuir and Freudlich isotherm models were implemented for the study of adsorption equilibrium (Ezzati, 2020; Rajahmundry *et al.*, 2021). Pseudo-first order and pseudo-second-order models were used for the kinetic study (Zhang *et al.*, 2020a). The thermodynamic study was done following Zhao *et al.* (2018) and Zhang *et al.* (2020a).

RESULTS AND DISCUSSION

In the concerned study, a carbonization temperature of 700°C, with activation time 1

h and activating agent phosphoric acid was used to obtain the desirable carbon. The estimated values of ash, moisture content and density have been illustrated in Fig. 1.

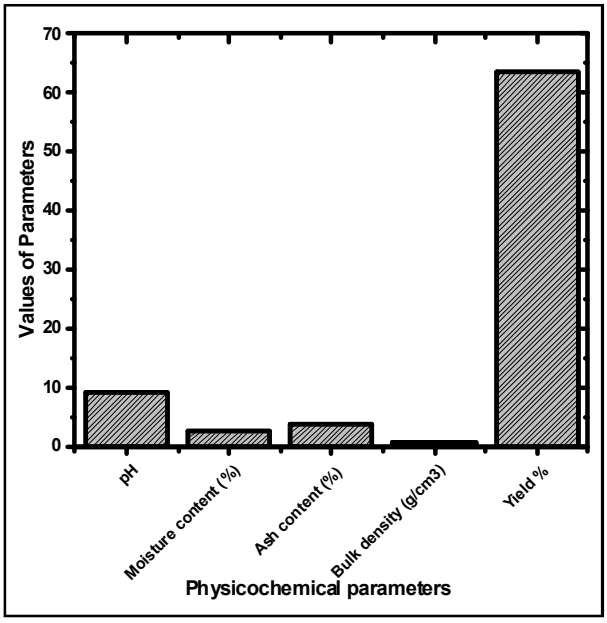

Fig. 1. Physico-chemical characteristics of coconut shell activated carbon (CSAC).

To analyze the yield per cent of carbon, masses of carbon before and after activation were calculated. The resulting masses were 115 and 71.5 g, respectively. Yield per cent was 73.1% and the overall process yield per cent of activated carbon obtained was 63.5%. Yield percentage with activation agent at an activation temperature of 700°C was interrelated to form a specific activated carbon. Phosphoric acid, impregnation ratio 1 : 3, activation time 1 h and activation temperature 700°C were used in the preparation of activated carbon.

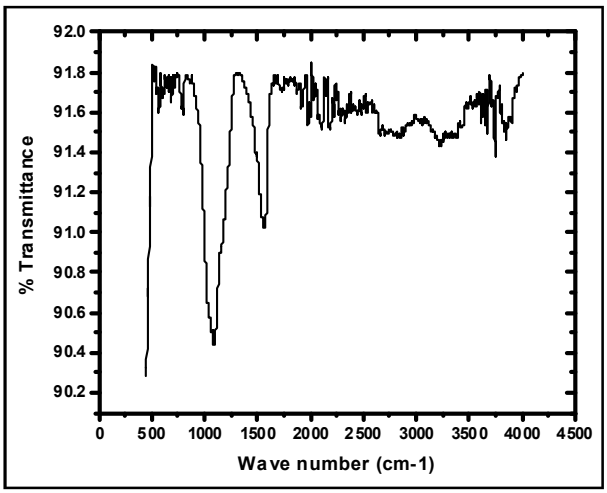

Fig. 2. FTIR spectra of coconut shell activated carbon (CSAC).

FTIR images of CSAC, prepared in the current study, had shown the surface chemistry of adsorbent (Fig. 2). The band at around 2400/cm (wave number) was observed and could be designated as an alkyne functional group. The C≡C stretching vibrations appeared in 2000 and 2100/cm; however, the carbon double bond was found at 1631/cm.

FESEM samples of activated coconut shell have been illustrated in Fig 3 i, ii and iii. The samples having cracked structure indicated the pyrolysis and activation of samples.

The impact of pH on the adsorption was analyzed by taking an extensive range of initial pH (2-10). The repercussion of initial pH on adsorption is shown in Fig. 4. The highest adsorption of DCM on CSAC was observed in between pH 6.0 and 8.0.

The effect of adsorbent dosage on the amount of dichloromethane (DCM) adsorbed at equilibrium on different adsorbents is shown

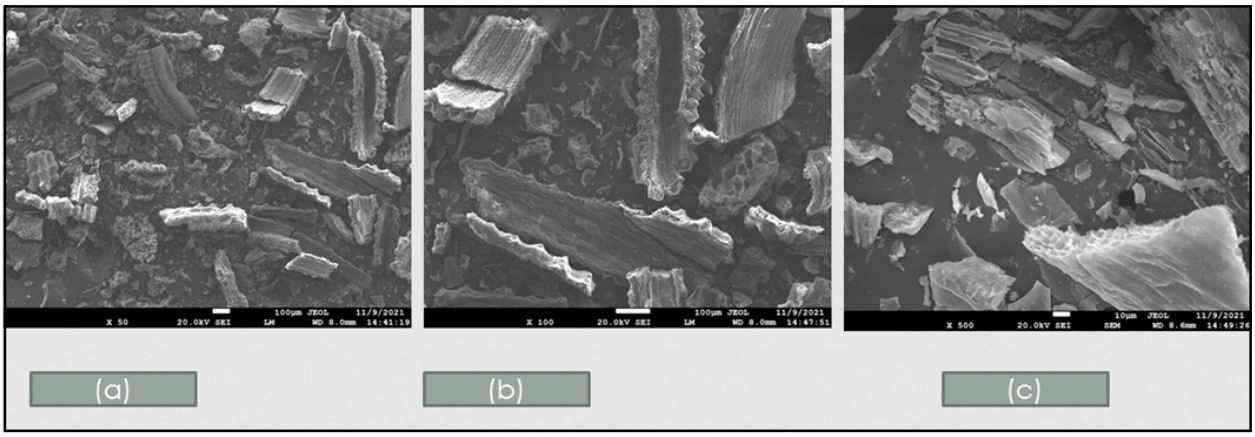

Fig. 3 i. FESEM images of coconut shell activated carbon (a-c).

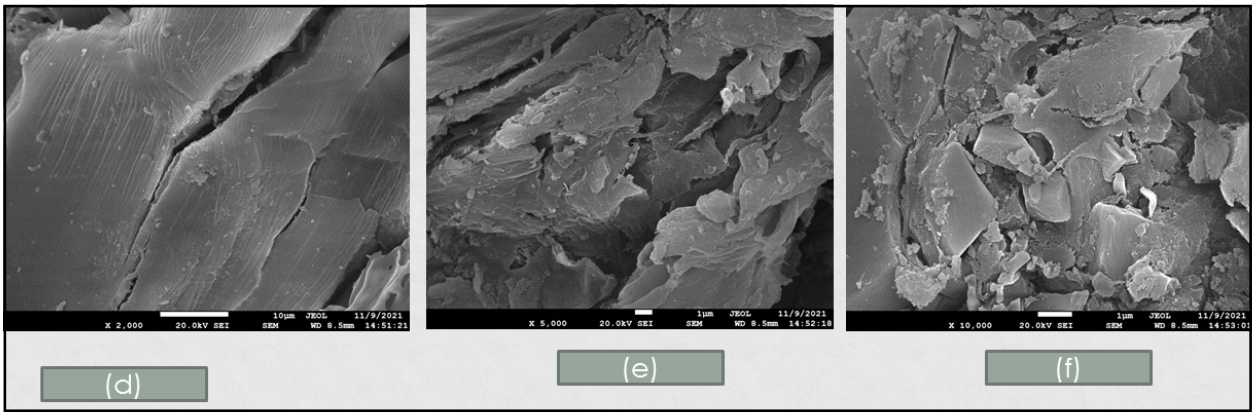

Fig 3 ii. FESEM images of coconut shell activated carbon (d-f).

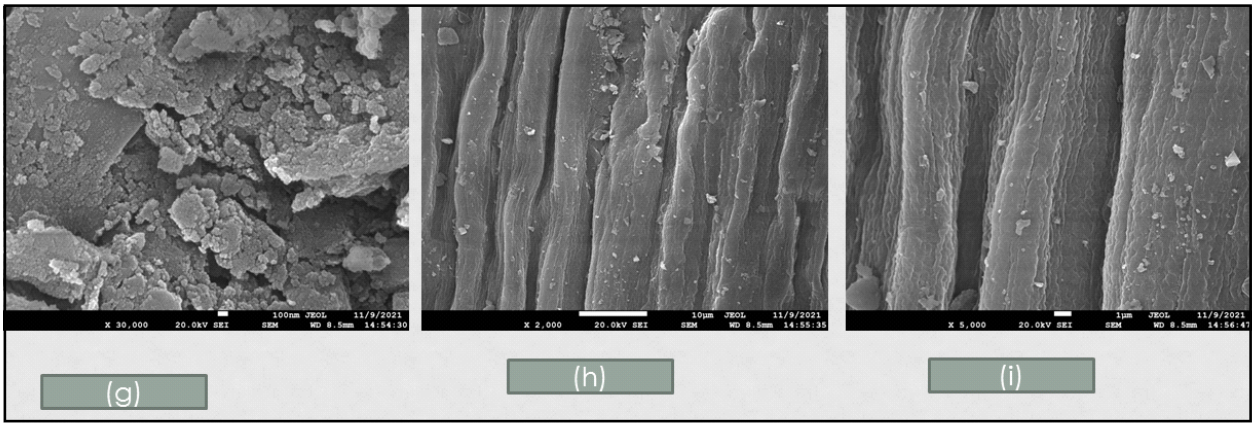

Fig 3 iii. FESEM images of coconut shell activated carbon (g-i).

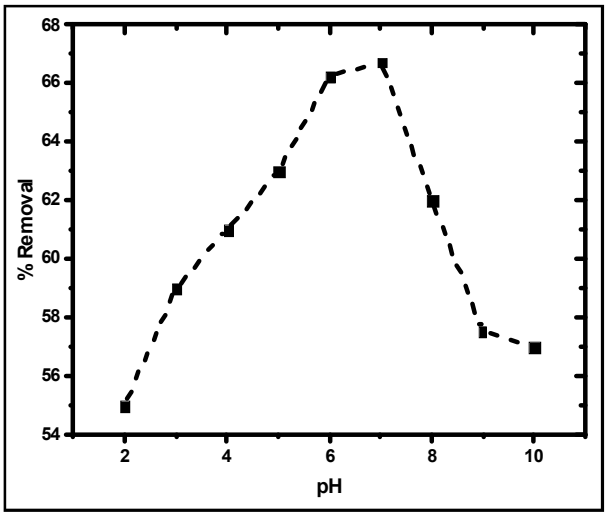

Fig. 4. Effect of initial pH on the percentage removal of DCM on coconut shell activated carbon (CSAC).

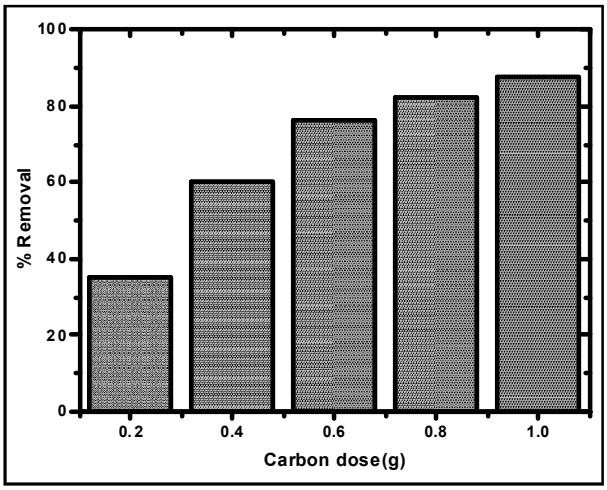

Fig. 5a. Effect of carbon dose on the % removal of DCM on coconut shell activated carbon (CSAC).

in Fig 5 (a) and (b). Adsorption doses were found to be directly proportional to per cent removal. Due to increase in surface area and accessibility of more adsorption sites, the adsorption percentage increased with increase in the adsorbent doses (Li *et al.*, 2020a; Zhang *et al.*, 2020b).

Adsorption increased with increase in initial DCM concentration. The concentration study was carried out at 25°C with a broad range of initial DCM concentrations (20-300 mg/l). The adsorption capacity of DCM was highest on CSAC (50.325 mg/g) at 300 mg/l at 25°C. It was observed that the adsorption process was

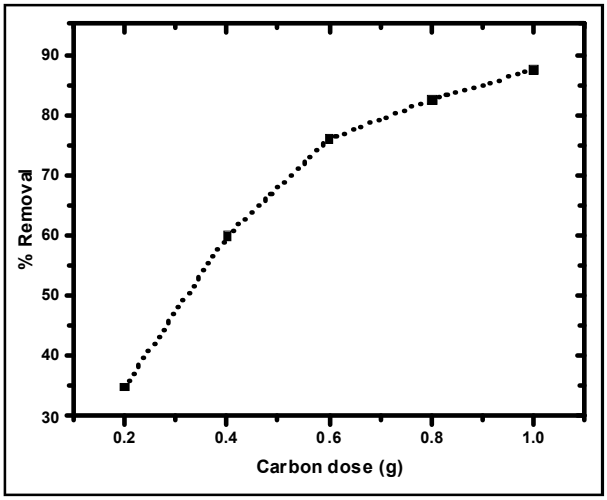

Fig. 5b. Effect of carbon dose on the percentage removal of DCM on coconut shell activated carbon (CSAC).

very speedy at low adsorbate concentration. Large pore size of CSAC was responsible for obtaining high adsorption capacity at high initial concentration of the adsorbate. On the other hand, at low adsorbate concentrations, the small sized and pore hydrophobicity were the controlling factors for getting high adsorption. On increasing the initial concentration of adsorbate, the adsorption capacity increased with the increase in the initial adsorbate concentration. As the concentration of the adsorbate increased, its movement on the surface of the adsorbent speeded up and finally it increased the adsorption capacity of the adsorbent (Ben-Ali *et al.*, 2017). On CSAC, dichloromethane (DCM) showed maximum adsorption capacity (50.32 mg/g).

Contact time had significant repercussions in the adsorption process. The contact time study for the adsorption of DCM on CSAC was carried out by taking 200 mg/l initial adsorbate concentration with constant pH at 25°C. It was observed that adsorption capacity increased with the increase in contact time. The maximum adsorption capacity on CSAC was 33 mg/g to 200 mg/l at 25°C (Fig. 6).

Experimental data in this study were analyzed by Langmuir and Freundlich isotherm models. By plotting the linear plot between Ce/qe vs. Ce, slope, intercept and qm values were calculated. The monolayer adsorption capacity value qm was highest for CSAC (48.42 mg/g) (Table 2). Slope and intercept were used for the calculation of K_f and n after plotting a linear

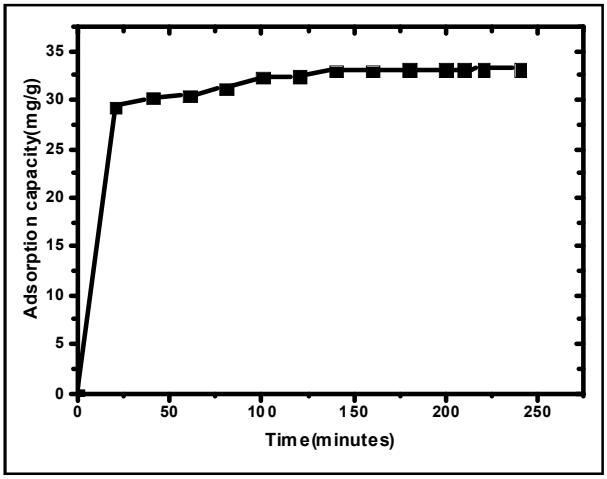

Fig. 6. Effect of contact time on the adsorption capacity of DCM on coconut shell activated carbon (CSAC).

plot of log qe vs. log Ce (Table 2). It illustrated the deviations from linearity, and the degree of heterogeneity in the adsorption sites. In the present study, the values of n were found to be n>1 for the sorption of dichloromethane on CSAC indicated a favorable adsorption. The regression coefficient (R^2) value showed better applicability of Freundlich model on CSAC (Li *et al.*, 2020a; Zhang *et al.*, 2020b).

Table 2. Langmuir and Freundlich constants for the adsorption of DCM on CSAC

Adsorbent	Langmuir constants			
CSAC	q max	K_L	R_L	R^2
	30.184	0.0503	0.498	0.84
Adsorbents	Freundlich constants			
CSAC	K_F	n		R^2
	1.592	1.376		0.97

The mechanism of adsorption was well elucidated by the pseudo first-order and pseudo-second-order rate equation. The value of pseudo-first-order was calculated from the slope and intercept of the linear plots. In pseudo-second-order-kinetics, the values of K_2 and qe (exp) were calculated from the slope and intercept of the linear plots of t/qt vs. t (Table 3). The correlation coefficient (R^2) value obtained for pseudo-first-order model did not represent a good fit with experimental data (Table 3). On the contrary, it followed the pseudo-second order kinetics model (Table 3) as evident from R^2 value calculated from the experimental data.

Table 3. Kinetic parameter for the adsorption of DCM on CSAC at 25°C (Co = 200 mg/l)

Adsorbent	Pseudo-first-order			Pseudo-second-order	
CSAC	qe	K_1	R^2	K_2	R^2
	6.17	-0.00011	0.87	0.008048	0.99

The thermodynamics parameters for the adsorption of dichloromethane (DCM) on CSAC have been illustrated in Table 4. The positive values of standard enthalpy change (ΔH°), predicted the spontaneity and endothermic nature of adsorption. The positive values of standard entropy change (Δ*S*°), explored the randomness in the adsorption process at the solid/solution interface. The values of ΔS° were negative, and it showed that the adsorption process was an endothermic and spontaneous reaction (Xie *et al.*, 2019; Xing *et al.*, 2019).

Table 4. Effect of concentration on the thermodynamics parameters for the adsorption of DCM at different temperature on CSAC

Concentration (mg/l)	ΔS° (J/K mol)	ΔH° (kJ/mol)	ΔG° (kJ/mol)
100			-17.302
	61.2072	19.6612	-18.2201
			-18.8321
200			-11.6301
	41.1462	14.2131	-12.2473
			-12.6588
300			-7.47738
	26.4562	14.2131	-7.87423
			-8.13879

CONCLUSION

The positive attributes such as physical resistance, adsorption properties, surface chemistry, reasonable cost and recovery of the activating agent, made the carbon prepared from the plant's origin, the most preferred material in the adsorbent world. Coconut shell activated carbon produced with impregnation ratio of 1 : 3, activation temperature at 700°C and activation time of 1 h. The present study showed that the adsorption process of dichloromethane on CSAC was influenced by temperature, pH and concentration of adsorbate, dosage of adsorbent and contact time. The adsorption was found to be maximum 50.5 mg/g for CSAC at pH range 6.0-8.0. The adsorption increased with increase in contact time and the temperature. The Langmuir model didn't fit well on CSAC for the adsorption of dichloromethane. Rather it went well with the Freundlich model. Kinetic data had shown the applicability of the pseudo-second-order. The R_L value between 0 and 1 for the adsorption of dichloromethane, favoured the adsorption. The adsorption of dichloromethane on CSAC was considered spontaneous. Standard entropy changes with positive value showed the increase in entropy, therefore, it confirmed randomness of the system. This study revealed that satisfying removal efficiencies of dichloromethane could be achieved by using coconut shell activated carbon (CSAC) as adsorbent.

REFERENCES

Alhooshani, K. R. (2019). Adsorption of chlorinated organic compounds from water with cerium oxide-activated carbon composite. *Arabian J. Chem.* **12**: 2585-2596.

Asejeje, G. I., Ipeaiyeda, A. R. and Onianwa, P. C. (2021). Occurrence of BTEX from petroleum hydrocarbons in surface water, sediment and biota from Ubeji Creek of Delta State, Nigeria. *Environ. Sci. Poll. Res.* **28**: 15361-15379.

Basu, S., Ghosh, G. and Saha, S. (2018). Adsorption characteristics of phosphoric acid induced activation of bio-carbon: Equilibrium, kinetics, thermodynamics and batch adsorber design. P*rocess Safety Environ. Prot.* **117**: 125-142.

Ben-Ali, S., Jaouali, I., Souissi-Najar, S. and Ouederni, A. (2017). Characterization and adsorption capacity of raw pomegranate peel biosorbent for copper removal. *J. Cleaner Prod.* **142**: 3809-3821.

Cen, J., Wei, S., Nan, H., Xu, J., Huang, Z., Liu, S., Hu, Q., Yan, J. and Ouyang, G. (2018). Incorporation of carbon nanotubes into graphene for highly efficient solid-phase microextraction of benzene homologues. *Microchemical J.* **139**: 203-209.

Ezzati, R. (2020). Derivation of pseudo-first-order, pseudo-second-order and modified pseudo-first-order rate equations from Langmuir and Freundlich isotherms for adsorption. *Chem. Eng. J.* **392**: 123705.

Gang, D., Ahmad, Z. U., Lian, Q., Yao, L. and Zappi, M. E. (2021). A review of adsorptive remediation of environmental pollutants from aqueous phase by ordered mesoporous carbon. *Chem. Eng. J.* **403**: 126286.

Hao, Z., Wang, C., Yan, Z., Jiang, H. and Xu, H. (2018). Magnetic particles modification of coconut shell-derived activated carbon and biochar for effective removal of phenol from water. *Chemosphere* **211**: 962-969.

Heidarinejad, Z., Dehghani, M. H., Heidari, M., Javedan, G., Ali, I. and Sillanpää, M. (2020). Methods for preparation and activation of activated carbon: A review. *Environ. Chem. Letters* **18**: 393-415.

Hernández-Fernández, J., Lopez-Martinez, J. and Barceló, D. (2021). Quantification and elimination of substituted synthetic phenols and volatile organic compounds in the wastewater treatment plant during the production of industrial scale polypropylene. *Chemosphere* **263**: 128027.

Ismail, I. S., Rashidi, N. A. and Yusup, S. (2022). Production and characterization of bamboo-based activated carbon through single-step H_3PO_4 activation for CO_2 capture. *Environ. Sci. Poll. Res.* **29**: 12434-12440.

Jian, X., Zhuang, X., Li, B., Xu, X., Wei, Z., Song, Y. and Jiang, E. (2018). Comparison of characterization and adsorption of biochars produced from hydrothermal carbonization and pyrolysis. *Environ. Tech. Inn.* **10**: 27-35.

Lam, S. S., Liew, R. K., Wong, Y. M., Yek, P. N. Y., Ma, N. L., Lee, C. L. and Chase, H. A. (2017). Microwave-assisted pyrolysis with chemical activation, an innovative method to convert orange peel into activated carbon with improved properties as dye adsorbent. *J. Cleaner Prod.* **162**: 1376-1387.

Li, X., Zhang, L., Yang, Z., Wang, P., Yan, Y. and Ran, J. (2020a). Adsorption materials for volatile organic compounds (VOCs) and the key factors for VOCs adsorption process : A review. *Sep. Pur. Tech.* **235**: 116213.

Li, Y. H., Chang, F. M., Huang, B., Song, Y. P., Zhao, H. Y. and Wang, K. J. (2020b). Activated carbon preparation from pyrolysis char of sewage sludge and its adsorption performance for organic compounds in sewage. *Fuel* **266**: 117053.

Li, Z., Li, Y. and Zhu, J. (2021). Straw-based activated carbon: Optimization of the preparation procedure and performance of volatile organic compounds adsorption. *Materials* **14**: 3284.

Liang, Q., Liu, Y., Chen, M., Ma, L., Yang, B., Li, L. and Liu, Q. (2020). Optimized preparation of activated carbon from coconut shell and municipal sludge. *Materials Chem. Phy.* **241**: 122327.

Lv, Z., Wang, H., Chen, C., Yang, S., Chen, L., Alsaedi, A. and Hayat, T. (2019). Enhanced removal of uranium (VI) from aqueous solution by a novel Mg-MOF-74-derived porous MgO/carbon adsorbent. *J. Colloid Interface Sci.* **537**: A1-A10.

Mahmoud, A. S., Mostafa, M. K. and Peters, R. W. (2021). A prototype of textile wastewater treatment using coagulation and adsorption by Fe/Cu nanoparticles: Techno-economic and scaling-up studies. *Nanomaterials Nanotechnology* **11**: 18479804211041181.

Nayak, A., Bhushan, B., Gupta, V. and Sharma, P. (2017). Chemically activated carbon from lignocellulosic wastes for heavy metal wastewater remediation : Effect of activation conditions. *J. Colloid Interface Sci.* **493**: 228-240.

Rajahmundry, G. K., Garlapati, C., Kumar, P. S., Alwi, R. S. and Vo, D. V. N. (2021). Statistical analysis of adsorption isotherm model and its appropriate selection. *Chemosphere* **276**: 130176.

Singh, J., Basu, S. and Bhunia, H. (2019). Dynamic CO_2 adsorption on activated carbon adsorbents synthesized from polyacrylonitrile (PAN): Kinetic and isotherm studies. *Microporous and Mesoporous Mat.* **280**: 357-366.

Soleimanpour, A., Farsi, M., Keshavarz, P. and Zeinali, S. (2021). Modification of activated carbon by MIL-53 (Al) MOF to develop a composite framework adsorbent for CO_2 capturing. *Environ. Sci. Poll. Res.* **28**: 37929-37939.

Udyani, K. and Purwaningsih, D. (2021). Chemical and physical activation using a microwave to increase the ability of activated carbon to adsorb dye waste. *Paper Presented at the Journal of Physics: Conference Series.*

Wen, X., Liu, H., Zhang, L., Zhang, J., Fu, C., Shi, X., Chen, X., Mijowska, E., Chen, M. J. and Wang, D. Y. (2019). Large-scale converting waste coffee grounds into functional carbon materials as high-efficient adsorbent for organic dyes. *Bioresource Tech.* **272**: 92-98.

Xie, Y., Chen, C., Ren, X., Wang, X., Wang, H. and Wang, X. (2019). Emerging natural and tailored materials for uranium-contaminated water treatment and environmental remediation. *Prog. Mat. Sci.* **103**: 180-234.

Xing, X., Jiang, W., Li, S., Zhang, X. and Wang, W. (2019). Preparation and analysis of straw activated carbon synergetic catalyzed by $ZnCl_2$-H_3PO_4 through hydrothermal carbonization combined with ultrasonic assisted immersion pyrolysis. *Waste Man.* **89**: 64-72.

Yagmur, H. K. and Kaya, I. (2021). Synthesis and characterization of magnetic $ZnCl_2$-activated carbon produced from coconut shell for the adsorption of methylene blue. *J. Mol. Stru.* **1232**: 130071.

Zhang, Z., Jiang, C., Li, D., Lei, Y., Yao, H., Zhou, G., Wang, K., Rao, Y., Liu, W. and Xu, C. (2020a). Micro-mesoporous activated carbon simultaneously possessing large surface area and ultra-high pore volume for efficiently adsorbing various VOCs. *Carbon* **170**: 567-579.

Zhang, Z., Lei, Y., Li, D., Zhao, J., Wang, Y., Zhou, G., Yan, C. and He, Q. (2020b). Sudden heating of H_3PO_4-loaded coconut shell in CO_2 flow to produce super activated carbon and its application for benzene adsorption. *Ren. Ener.* **153**: 1091-1099.

Zhao, X., Li, X., Zhu, T. and Tang, X. (2018). Adsorption behaviour of chloroform, carbon disulfide, and acetone on coconut shell-derived carbon: Experimental investigation, simulation and model study. *Environ. Sci. Poll. Res.* **25**: 31219-31229.

Zhu, L., Shen, D. and Luo, K. H. (2020). A critical review on VOCs adsorption by different porous materials: Species, mechanisms and modification methods. *J. Hazardous Mat.* **389**: 122102.