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One-step chemical modification of pine cones for the removal of methyl orange from aqueous media

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Water pollution is a significant and serious problem because it poses an enormous threat to the environment. Agricultural materials may emerge as an elegant solution to overcome this problem. In this study, a carbonaceous adsorbent from Aleppo pine cones was prepared by chemical modification using a simple chemical treatment with sulfuric acid. The adsorption process is extremely influenced by the operating conditions. The optimal elimination of methyl orange was achieved at a concentration of 50 mg/L, an adsorbent dosage of 0.12 g, an adsorption time of 50 min, and a temperature of 25 °C. The spontaneous exothermic behavior of the removal system was proved by the negative values of ΔG and ΔH, respectively. The kinetic representation by employing a pseudo-second order equation demonstrates consistency of the adsorption data with the supreme correlation coefficient close to unity. The isotherm investigation reveals that the Langmuir equation is most applicable to presenting the removal experimental data. These results emphasize that modified Aleppo pine corn powder can act as an interesting adsorbent for eliminating methyl orange from untreated contaminated water.

Keywords: Chemical treatment, Water pollution, Methyl orange, Aleppo pine cones.

INTRODUCTION

Water treatment results in significant financial losses because it requires an effective method to eliminate the contaminated materials that pose a critical intimidation to the environment and living things. With the fast growth in the industry fields to meet human needs, the amount of industrial hazardous waste is also growing, and dyes can represent one of the main pollutants that contaminate water bodies [1]. Dyes are chemical compounds that play a major role in the textile industry. They can pose a manifested threat to the water circumference if subtracted without any handling [2]. Therefore, an efficient removal of dyes is highly important.

New policies concerning the environment have obliged factories to utilize methods that can minimize the size of waste that they deposit into the environment [3]. The strategy taken to reduce water contamination is to remove the contaminated materials from the water. Various sophisticated wastewater remediation techniques have been applied to the elimination of pollutants, including photo catalysis [4], coagulation [5], electro Fenton [6], electrochemical filtration [7], and adsorption [8]. Adsorption is considered an efficient, simple and easy-to-control technique to treat emerging water contaminants, and it plays a substantial role in environmental redemption [9]. Adsorption is often used for reducing contamination by adding adsorbent materials to the contaminated medium.

Agricultural materials are considered a viable alternative adsorbent in the adsorption technology being environmentally friendly, available, and of low economic cost [10]. Their unique chemical composition contains various compounds, including cellulose, hemicellulose and lignin. These compounds can adsorb a variety of contaminated species and can greatly improve the removal of aquatic pollutants [11]. Aleppo pine is a natural tree widely propagated in the Mediterranean countries due to its unique properties, such as adaptability and rapid and abundant production [12]. Enormous quantities of remains (needles, cones, branches and bark) will be generated as a result of logging the trees. These low-value wastes need sustainable processing in order to mutate into more valuable substances [13].

Although agricultural materials as adsorbents can give a passable ability in removing pollutants, their use is still lower than that of porous carbon material [14]. This may be a substantial limitation for their employment in water treatment [15]. The necessity to reduce the amount of contaminated materials led to the search for ways to improve the adsorption process. Chemical treatment of agricultural materials [16-19] is one way that is used in

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adsorption technology that improves the adsorbent surface by using a proper activation agent. Sulfuric acid (H_2SO_4) is an excellent oxidizing agent that is used continually for the production of carbonaceous materials with a rich oxygen content of the surface active groups such as carboxylic and hydroxylic groups [17].

The purpose of this research is to prepare a carbonaceous adsorbent from Aleppo pine cones using a simple chemical treatment method and to examine the influence of chemically modified Aleppo pine cone powder on the elimination of methyl orange dye from untreated contaminated water.

EXPERIMENTAL

Chemicals

The chemicals in this study were utilized as obtained without any additional purification. Methyl orange (MO) of analytical grade was acquired from Fluka. Its chemical formula is $C_{14}H_{14}N_3NaO_3S$, M. Wt. 327.33 g/mol, and it absorbs at λ_{max} of 464 nm [20]. Sulfuric acid was supplied by Sigma Aldrich.

Preparation of the adsorbent

The Aleppo pine cones were collected from Duhok, Iraq. They were cut into little pieces, rinsed thoroughly with distilled water (DW) so as to remove any dust or impurities, and dried using a drying oven (LabTech, Korea) at 100 °C for 6 h. The dried material was grinded using an electric food grinder, and then sieved by a molecular sieve to gain Aleppo pine cone powder with small particles not more than 150 μm.

The modification of Aleppo pine cones by sulfuric acid was carried out at room temperature for 24 h. Firstly, 20 g of the Aleppo pine cone powder was put in a beaker. 50 ml of concentrated H_2SO_4 was added to the powder and mixed mechanically for 1 h. The blend was then left at 25 °C for 24 h, and the resulting black product was filtered and thoroughly rinsed with DW. The obtained black solid was then dried for 4 h at 100 °C. The chemically modified Aleppo pine cone powder was labelled as CAPC, and was characterized using Fourier transform infrared spectrometry on a Shimadzu, Japan instrument, and field emission scanning electron microscopy (Mira 3, TESCAN microscope).

Adsorption experiments

A batch method was utilized in this investigation to examine the adsorption properties of CAPC toward methyl orange. The adsorption experiment setup was performed using 25 mL of the desired methyl orange solution. Various parameters were investigated using one-variable approach on a time procedure to define the optimal removal conditions. The variables included: amount of carbonaceous Aleppo pine cones (0.02, 0.04, 0.06, 0.08, 0.1, 0.12, 0.15, and 0.2 g), concentration of methyl orange (25, 50, 75, 100, 125, and 150 mg/L), temperature of the adsorption system (298, 308, 318, 328 K), and uptake time (10, 20, 30, 40, 50, 60, 80, and 100 min.). The solutions (suspensions) were agitated continuously in a heated shaking bath (GFL, Germany) and then separated at a speed of 3000 rpm in a centrifuge 8-tubes (Gallenkamp, England) to gain a clear supernatant. The concentration of methyl orange residual was estimated by ultraviolet-visible spectroscopy (UV-1800, Shimadzu) at 464 nm. The value of methyl orange adsorbance onto CAPC was estimated from the concentration variance.

The adsorption capacity at equilibrium (q_e) was recorded from equation (1), and the removal efficiency (% R) was determined from equation (2).

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

$$\% R = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

where C_0 and C_e represent the starting and equilibrium MO concentration in mg/L, V symbolizes the volume of MO solution in L, and m refers to the CAPC amount in g.

The thermodynamic parameters for the MO dye adsorption onto the CAPC surface were estimated from equations (3) and (4):

$$\Delta G^{\circ} = -RT \ln K \tag{3}$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{4}$$

where K is the equilibrium constant, T is the absolute temperature (K), and R is the gas constant ($8.314\ J\ K^{-1}\ mol^{-1}$).

In addition, four equations were applied in the kinetic investigation: pseudo-first order (equation 5), pseudo-second order (equation 6), intra-particle diffusion (equation 7), and Elovich model (equation 8).

$$\ln(q_e - q_t) = \ln q_e - k_1\, t \tag{5}$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2\, q_e^2}\right) + \left(\frac{1}{q_e}\right) t \tag{6}$$

$$q_t = k_{int}\, t^{1/2} + C \tag{7}$$

$$q_t = \left(\frac{1}{\beta}\right) \ln \alpha\beta + \left(\frac{1}{\beta}\right) \ln t \tag{8}$$

where q_e is the adsorption capacity at equilibrium, q_t is the adsorption capacity at time t, k_1 and k_2 are the PFO and PSO rate constants, respectively, k_{int} is the IPD constant, and α and β are the EV constants.

Finally, the isotherm analysis was performed by applying the Langmuir and the Freundlich models, whose linearized forms are displayed in equations (9) and (10), respectively.

$$\frac{1}{q_e} = \frac{1}{q_m\,K_L C_e} + \frac{1}{q_m} \qquad (9)$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (10)$$

where q_m represents the ultimate adsorption capacity, K_L denotes the Langmuir constant, and K_F and n symbolize the Freundlich constants.

RESULTS AND DISCUSSION

CAPC characterization

It was established that the existence of amine, hydroxyl, and carbonyl groups on the surface of the adsorbent materials can ameliorate the adsorption process [21-23]. The functional groups on the surface of carbonaceous Aleppo pine cone powder (CAPC) were detected using FT-IR spectrophotometry. The FT-IR spectra of CAPC are presented in Figure 1. Various bands between 461 – 781 cm^{-1} were recorded that were related to wagging vibration of C–H in aromatic compounds [24]. The peak at 1045 cm^{-1} may be attributed to the C–N stretching in amines [25]. The broad band at 1165 cm^{-1} can be assigned to C–C and C–O stretching vibrations in esters, alcohols, or phenols [26]. The prominent peak at 1626 cm^{-1} can be attributed to the C=C stretching of the aromatic ring [1]. The notable band at 1707 cm^{-1} represents the carbonyl group, which emphasizes the existence of aldehydes and carboxylic acids [9]. The wide band at 3416 cm^{-1} can be referred to the N–H vibration in amines [24]. The sharp band at 3616 cm^{-1} can be referred to the hydroxyl groups in alcohols and phenols [21].

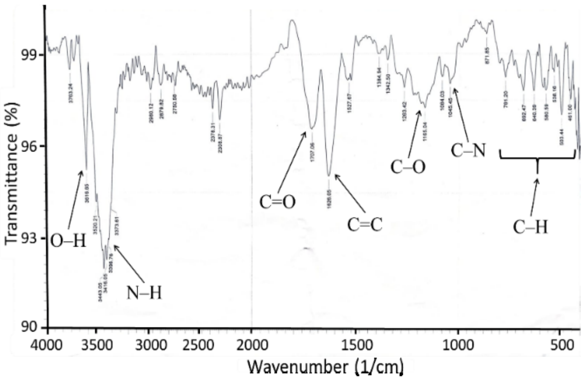

Fig. 1. FT-IR spectra of the CAPC surface.

The morphological analysis of CAPC was documented using a FESEM microscope. Figure 2 demonstrates the FESEM micrograph of the CAPC surface. A uniform surface containing adequate grooves can be observed, which can facilitate the transport of MO dye molecules within the CAPC particles and thus increase the removal process.

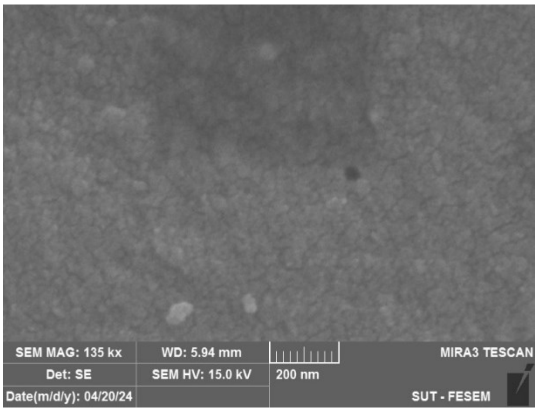

Fig. 2. FESEM image of the CAPC surface.

Adsorption study

One of the main variables that influences the removal of MO dye on the CAPC surface is the adsorbent amount. It was studied using various CAPC doses (between 0.02 – 0.2 g), 50 mg/L initial MO concentration, 50 min uptake time, at 25 °C. As seen in Figure 3, changing the adsorbent dose will affect the removal efficiency. A minimum removal efficacy of 32% was observed at a low adsorbent dosage, and the removal efficacy increases with the rise in the amount of adsorbent to accomplish its ultimate removal percentage of 94% using 0.12 g of CAPC. The reason for this increase is that at a fixed concentration of MO, increasing the CAPC dosage leads to a prominent increase in the free effective sites eligible for adsorption, which thus increases the removal efficacy. An additional increase in the adsorbent amount would show no significant improvement, which means that the uptake process attains its equilibrium state.

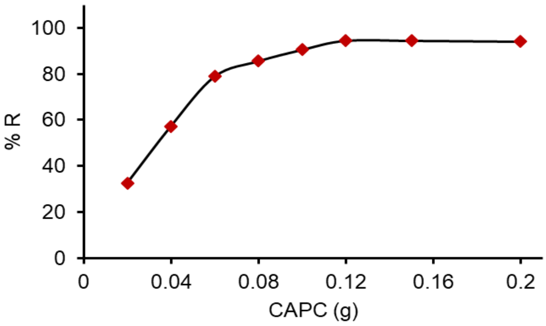

Fig. 3. Influence of the CAPC dosage on the elimination of MO dye.

The effectiveness of the experiment time on the uptake of MO dye on the CAPC surface was investigated with different adsorption times between 10 - 100 min, and 50 mg/L initial MO concentration, 0.12 g of CAPC mass, at 25 °C. Figure 4 shows a good uptake level at the beginning of the adsorption, that can be associated with the affinity between MO molecules and CAPC particles. Also, the removal efficiency increases as the contact time increases to accomplish its ultimate value of 94% at a time of 50 min, which can be considered as the removal equilibrium time. This is attributed to the fact that increasing the uptake time will give adequate time for MO molecules to be adsorbed on the available CAPC adsorption sites, which leads to the removal enhancement.

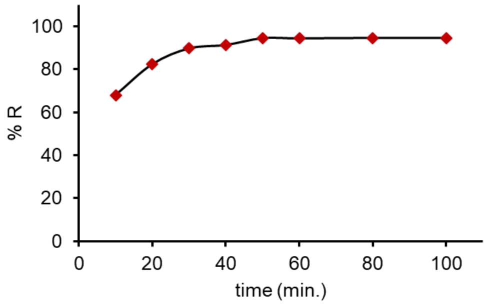

Fig. 4. Influence of time on the elimination of MO dye on the CAPC surface.

The impact of the starting MO dye concentration is presented in Figure 5. It was tested using varied initial MO concentrations (between 25 – 150 mg/L), 0.12 g CAPC doses, 50 min uptake time, at 25 °C. Figure 5 shows a decrease in the removal efficacy as the starting concentration of MO dye increases, which is referred to the presence of vacant efficient removal sites on the CAPC particle that are required to accommodate the molecules of MO dye. Increasing the initial MO dye concentration will provide more dye molecules that require more vacant sites, which reduces the removal efficiency.

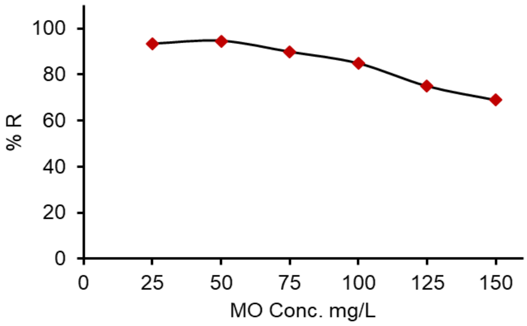

Fig. 5. Influence of the initial MO dye concentration on the elimination process.

The impact of the temperature on the uptake of MO dye onto the CAPC surface was also investigated at different temperatures (298, 308, 318, 328 K), 50 mg/L initial MO concentration, 0.12 g CAPC doses, and 50 min uptake time. Figure 6 displays a gradual decrease in the removal level with rising temperature. Increasing the temperature may provide more energy for MO molecules to be able to flee from the CAPC surface and return to the bulk solution, which will reduce the removal efficiency.

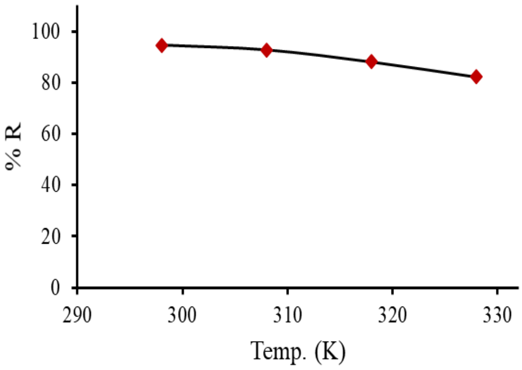

Fig. 6. Influence of the temperature on the elimination of MO dye on the CAPC surface.

Thermodynamic study

The thermodynamic assessment was carried out by analyzing the experimental data recorded from the temperature effect to calculate the essential thermodynamic parameters. These parameters are the Gibbs free energy change (ΔG) that can be estimated using equation (3), the entropy change (ΔS) and the enthalpy change (ΔH) that can be evaluated from the intercept and slope of the straight line obtained from the Van’t Hoff plot as shown in Figure 6. The results obtained are presented in Table 1.

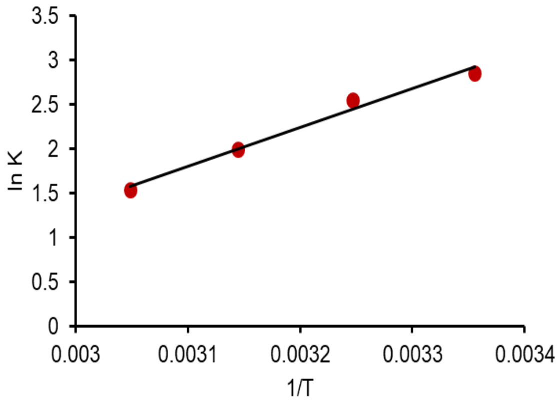

Fig. 7. Van’t Hoff plot for the removal of MO dye on the CAPC surface.

Table 1. Thermodynamic parameters of MO dye removal on the CAPC surface at diverse temperatures

T (K)	*ΔG°* *(kJ/mol)*	*ΔH* *(kJ/mol)*	*ΔS* *(J/mol K)*	*R^2*
298	-7.076	-3.654	-98.34	0.98
308	-6.514			
318	-5.282			
328	-4.186			

The negative value of ΔS clearly signifies a drop in the randomness that was fulfilled as a result of the linkage between the MO molecules and the CAPC particles. Also, the negative value of ΔH signifies that the behavior of the elimination system is exothermic. In addition, the spontaneous behavior of the removal process was evidenced by the negative value of ΔG, and raising the temperature will decrease the spontaneity of the MO molecules' elimination onto the CAPC surface.

Kinetic study

The kinetic study was performed by applying the linearized form of four kinetic equations to the data obtained from the contact time experiment: the pseudo-first order (PFO), the pseudo-second order (PSO), the intra-particle diffusion (IPD), and the Elovich model (EV), whose equations are given in equations (5) – (8), and their plots are displayed in Figure 8. The kinetic outcomes are recorded in Table 2.

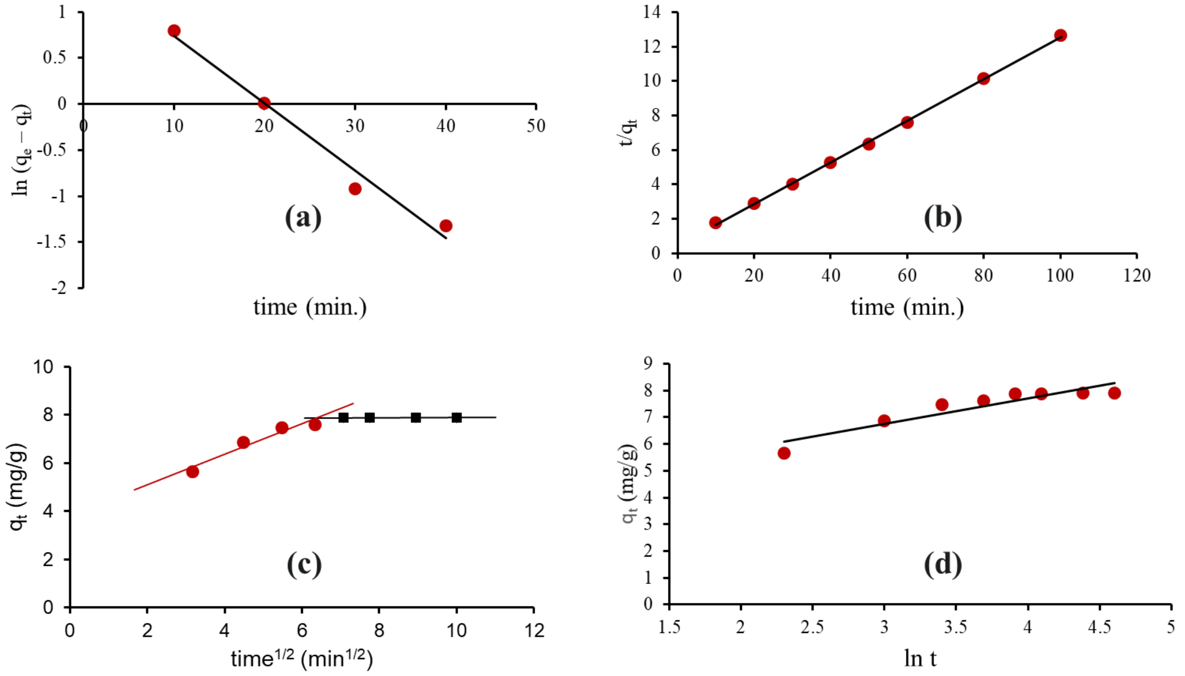

Fig. 8. Kinetic models (a) PFO, (b) PSO, (c) IPD, and (d) Elovich plots for the removal of MO dye on the CAPC surface.

Table 2. Kinetic parameters of MO dye removal on the CAPC surface

q_e exp.	*Pseudo-first order*			*Pseudo-second order*			*Intra-particle diffusion*			*Elovich*			
	k_1	q_e *cal.*	R^2	k_2	q_e *cal.*	R^2	k_{int}	q_e *cal.*	R^2	α	β	q_e *cal.*	R^2
7.88	0.16	4.33	0.97	0.03	8.24	0.99	0.63	8.73	0.93	61.36	1.11	7.48	0.85

Table 3. Isotherm parameters of MO dye removal on the CAPC surface

Langmuir model			*Freundlich model*		
k_L	q_m	R^2	K_F	n	R^2
0.14	21.32	0.93	0.05	0.45	0.87

The PSO kinetic equation displays a more compatible fit of the adsorption experimental data compared to the other models. The PSO model gives the greatest correlation coefficient (R^2) of 0.99 and the closest calculated removal capacity (q_e cal.) of 8.24 mg. g^{-1}. This confirms that the removal of MO molecules onto the CAPC surface obeys the kinetics of the PSO equation, and the removal process might be controlled by chemical adsorption. In addition, one of the interesting results is found when applying the IPD equation. Three steps were suggested to elucidate the adsorption system according to this model. Firstly, the boundary layer of the adsorbent outer surface experiences mass transfer and secondly, intra-particle diffusion across the interior adsorbent structure. The adsorption then takes place at the final step. Figure 8 (c) displays a nonlinear intra-particle diffusion plot over the entire time period, which denotes that more than one step is involved in the removal system. The vanishing of the first step in the IPD plot signifies that the outer adsorbent transfer is extremely fast, which can refer to the significant affinity between the MO molecules and the CAPC particles, as mentioned before, which leads to the intra-particle diffusion starting quickly.

Isotherm study

The isotherm analysis was conducted by employing two isotherm equations to the experimental data collected from the impact of initial MO concentration. The Langmuir and the Freundlich isotherms, whose mathematical expressions are used in this investigation, are shown in equations (9) and (10), respectively. The resulting parameters of these isotherms are recorded in Table 3.

From the results in Table 3 it is obvious that the Langmuir model is more proper than the Freundlich model for modeling the removal process. With the highest correlation coefficient of approximately 0.93, the Langmuir isotherm describes the monolayer formation of MO dye coverage on the homogeneous CAPC surface.

CONCLUSIONS

The present investigation examines the removal of methyl orange dye using chemically modified Aleppo pine cones. The removal behavior was illustrated with the alteration in the process-affected factors. The adsorption study reveals that the optimum operating variables were found to be 0.12 g of the modified biosorbent CAPC, 50 min contact time to attain equilibrium, adsorption temperature of 25 °C, and 50 mg/L of starting MO concentration. The thermodynamic assessment reveals that the removal system is exothermic and spontaneous. The kinetic study demonstrates that the best fit of the adsorption data was achieved by applying the pseudo-second order equation. The isotherm study validates that the Langmuir model is more acceptable to depict the uptake system. This investigation provides premeditation into the use of modified agricultural material in the removal process and offers direction for further exploration of new biosorbents to modulate the uptake level of pollutants from water.

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REFERENCES

1. O. S. Ali, D. E. AL-Mammar, *Iraqi J. Sci.*, **65**, 1824 (2024).
2. N. Samghouli, L. Rghioui, S. Sebbahi, A. El Hajji, L. Guennoun, R. Khaoulaf, M. S. Idrissi, S. El Hajjaji, *Bulg. Chem. Commun.*, **57**, 85 (2025).
3. S. Karishma, V. C. Deivayanai, P. Thamarai, A. Saravanan, P. R. Yaashikaa, *Sustain. Chem. Environ.*, **7**, 100143 (2024).
4. K. Tohdee, S. Mukjinda, S. Semmad, A. Jotisankasa, P. Praserthdam, B. Jongsomjit, *J. Taiwan Inst. Chem. Eng.*, **142**, 104670 (2023).
5. B. Narindri Rara Winayu, C. C. Chou, H. Chu, *J. Taiwan Inst. Chem. Eng.*, **139**, 104529 (2022).
6. A. Hadadi, A. Imessaoudene, J. C. Bollinger, A. Bouzaza, A. Amrane, H. Tahraoui, L. Mouni, *J. Environ. Manage.*, **331**, 117286 (2023).
7. Z. Cao, Q. Li, P. Yan, X. Jing, J. Zhang, *J. Taiwan Inst. Chem. Eng.*, **161**, 105537 (2024).
8. K. Qi, M. Chen, R. Dai, Q. Li, M. Lai, Z. Wang, *Water (Switzerland)*, **12**, 1 (2020).
9. S. M. Al-Mahmoud, *Egypt. J. Chem.*, **63**, 2947 (2020).
10. S. T. Nipa, N. R. Shefa, S. Parvin, M. A. Khatun, M. J. Alam, S. Chowdhury, M. A. R. Khan, S. M. A. Z. Shawon, B. K. Biswas, M. W. Rahman, *Results Eng.*, **17**, 100857 (2023).
11. A. Bhatnagar, M. Sillanpää, A. Witek-Krowiak, *Chem. Eng. J.*, **270**, 244 (2015).
12. Y. Zhou, J. Lu, Y. Zhou, Y. Liu, *Environ. Pollut.*, **252**, 352 (2019).
13. A. N. Olaimat, A. M. Ababneh, M. Al-Holy, A. Al-Nabulsi, A. A. Qatatsheh, Z. W. Jaradat, B. A. Albiss, T. Osaili, R. A. Holley, *Food Control*, **164**, 110587 (2024).
14. M. Chebbi, S. Ounoki, L. Youcef, A. Amrane, *J. Ind. Eng. Chem.*, **126**, 327 (2023).
15. V. C. G. Dos Santos, J. V. T. M. De Souza, C. R. T. Tarley, J. Caetano, D. C. Dragunski, *Water. Air. Soil Pollut.*, **216**, 351 (2011).

16. D. Schwantes, A. C. Gonçalves, G. F. Coelho, M. A. Campagnolo, D. C. Dragunski, C. R. T. Tarley, A. J. Miola, E. A. V. Leismann, *J. Chem.*, **2016**, 1 (2016).
17. M. Bhaumik, H. J. Choi, M. P. Seopela, R. I. McCrindle, A. Maity, *Ind. Eng. Chem. Res.*, **53**, 1214 (2014).
18. A. H. Jawad, R. A. Rashid, M. A. M. Ishak, K. Ismail, *J. Taibah Univ. Sci.*, **12**, 809 (2018).
19. A. H. Jawad, A. S. Abdulhameed, M. S. Mastuli, *J. Taibah Univ. Sci.*, **14**, 305 (2020).
20. I. A. W. Khalaf, S. M. Al-Mahmoud, *Macromol. Symp.*, **414**, 2400223 (2025).
21. S. Rattanapan, J. Srikram, P. Kongsune, *Energy Procedia*, **138**, 949 (2017).
22. M. J. Ahmed, M. A. Islam, M. Asif, B. H. Hameed, *Bioresour. Technol.*, **243**, 778 (2017).
23. A. H. Jawad, Y. S. Ngoh, K. A. Radzun, *J. Taibah Univ. Sci.*, **12**, 371 (2018).
24. K. Mabalane, N. D. Shooto, P. M. Thabede, *Case Stud. Chem. Environ. Eng.*, **10**, 100782 (2024).
25. M. Choudhary, R. Kumar, S. Neogi, *J. Hazard. Mater.*, **392**, 122441 (2020).
26. A. A. Alsarayreh, S. A. Ibrahim, S. J. Alhamd, T. A. Ibrahim, M. N. Abbas, *Karbala Int. J. Mod. Sci.*, **10**, 511 (2024).
27. Y. Raji, A. Nadi, I. Mechnou, M. Saadouni, O. Cherkaoui, S. Zyade, *Diam. Relat. Mater.*, **135**, 109834 (2023).