JEE Journal of Ecological Engineering

Journal of Ecological Engineering, 2025, 26(5), 102–113
https://doi.org/10.12911/22998993/200637
ISSN 2299–8993, License CC-BY 4.0

Received: 2025.01.27
Accepted: 2025.02.24
Published: 2025.03.16

Adsorption of SDBS-MBAS from aqueous solutions using natural zeolite and activated carbon: A comparative study

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ABSTRACT

This study evaluates the performance of natural Jordanian zeolite and activated carbon for the removal of methylene blue active substances (MBAS) from carwash water, focusing on sodium dodecyl benzene sulfonate (SDBS), the primary component of MBAS. Comparative adsorption experiments with activated carbon were conducted under controlled conditions (pH 6.8, 25 °C) to assess removal efficiency. Adsorption isotherms were constructed using multiple adsorbent dosages (0.1 to 2.0 g) and varying contact times (5 to 120 minutes) to determine maximum adsorption capacities and evaluate adsorption mechanisms. Optimization results revealed that the most efficient removal for zeolite (95.79%) was achieved at a 2.0 g dosage and a 60-minute contact time, whereas activated carbon attained a maximum removal efficiency of 99.21% under optimal conditions (2.0 g dosage, 50-minute contact time). At lower dosages (1.0 g), zeolite achieved 93.68% removal in 60 minutes, while activated carbon required only 30 minutes to reach 98.42%. When considering cost-effectiveness, natural zeolite being locally abundant and significantly less expensive than activated carbon, achieved near-optimal removal at a dosage of 1.0 g, making it a more economically viable option despite slightly lower efficiency. Removal efficiency for both materials increased with higher dosages, elevated temperatures, and lower initial SDBS concentrations. Thermodynamic analysis revealed that the adsorption process was spontaneous and endothermic, with Gibbs free energy (ΔG°) values favoring zeolite over activated carbon. Isotherm modeling indicated that adsorption data for natural zeolite fit well with both the Langmuir and Freundlich models, while activated carbon aligned more closely with the Langmuir and Pseudo-second-order models. Sorption isotherms revealed maximum adsorption capacities derived from the Langmuir model, with natural zeolite capacity increasing from 24% to 31% as the temperature rose from 25 °C to 45 °C and activated carbon showing a corresponding increase from 11% to 22%. These findings highlight the potential of natural volcanic tuff, an abundant and cost-effective form of zeolite in Jordan, as a sustainable alternative to activated carbon for MBAS removal from carwash wastewater.

Keywords: natural zeolite, activated carbon, MBAS, SDBS, pseudo-model; langmuir mode, thermodynamic.

INTRODUCTION

Water scarcity is a critical challenge in Jordan, where the population has grown from 9.5 million in 2015 to 11.4 million in 2023, significantly increasing water demand without a corresponding rise in supply (Bdour et al., 2008; Abdallat et al., 2024; Bakacs et al. 2013). Traditional car washes consume large amounts of water and generate wastewater containing pollutants like phosphates and petroleum-based chemicals, which harm aquatic ecosystems and public health. Solid waste and toxic gas emissions from car washing also contribute to environmental pollution (Lin et al., 2011; Canales et al., 2021).

To address these challenges, wastewater recycling techniques, particularly for carwash water, have gained attention (Canales et al., 2021). Natural zeolite is recognized as an effective adsorbent for removing contaminants such as heavy metals, pharmaceutical residues, and sodium dodecyl benzene sulfonate (SDBS), a common

anionic surfactant used in detergents. Excessive SDBS discharge can cause eutrophication and toxicity in aquatic systems. Studies have shown that surfactant-modified zeolites enhance adsorption efficiency for pollutants (Mahvi et al., 2016, Sarıci et al., 2022). Zeolite's effectiveness in removing ammonium, phosphorus, and heavy metals, along with its potential for constructed wetland applications, highlights its versatility (Shi et al., 2018; Kharabsheh et al., 2025).

Activated carbon (AC) is another effective adsorbent, with studies demonstrating its capacity to remove dyes, surfactants, and other pollutants from wastewater. For example, AC modified with anionic surfactants has shown improved methylene blue adsorption (Kuang, et al., 2020), while its application to carwash wastewater has resulted in significant reductions in TSS, BOD, COD, and MBAS levels (Kowsalya et al., 2020, Saad et al., 2024).

Kuang et al. (2020) explored the enhanced adsorption of methylene blue (MB) dye ions on activated carbon (AC) modified with three surfactants in aqueous solutions. The study utilized anionic surfactants; sodium lauryl sulfate (SLS) and sodium dodecyl sulfonate (SDS), and a cationic surfactant; hexadecyl trimethyl ammonium bromide (HTAB). Their findings revealed that the adsorption performance of cationic dye on activated carbon modified with anionic surfactants (SLS) was significantly improved, whereas it was reduced when modified with a cationic surfactant (HTAB) (Kuang, et al., 2020).

In Jordan, where natural zeolite is abundant and economically accessible, the need for regeneration is less critical compared to regions with limited resources (Kharabsheh and Bdour, 2025). Regeneration techniques, such as thermal treatment, chemical washing with acids or bases, and ion exchange, are commonly used to restore the adsorption capacity of zeolite (Shi et al., 2018; Kharabsheh et al., 2025). However, these methods can be costly, energy-intensive, and may cause structural degradation of the material over time, reducing its long-term efficiency. Considering Jordan's significant natural zeolite reserves, it is often more practical and cost-effective to utilize fresh zeolite rather than investing in regeneration processes, making it a viable and sustainable option for applications like wastewater treatment.

This study hypothesizes that Jordanian natural zeolite offers an economical and environmentally friendly alternative for surfactant removal, with adsorption efficiency reaching 93%, slightly lower than the 98% of activated carbon. The objectives include comparing the adsorption capacities of natural zeolite and activated carbon under various conditions (pH, temperature, dosage, mixing time), analyzing adsorption isotherms and kinetics (Langmuir, Freundlich, Pseudo-second order), and conducting thermodynamic analyses to assess the process's spontaneity and endothermic nature. The findings aim to promote the use of natural volcanic tuff as a cost-effective solution for sustainable wastewater treatment.

MATERIALS AND METHODS

Materials

Natural zeolite, sourced from Jabal Artin (30 km northeast of Al-Mafraq, Jordan), was ground, sieved to <45 μm particles, and used for adsorption experiments. Zeolites are aluminosilicate minerals with high cation exchange capacities due to their loosely bound Na^+, K^+, Ca^{2+}, or Mg^{2+} ions (Kandah et al. 2006). Activated carbon, derived from Jordanian asphalt, was chemically activated with sulfuric and nitric acids at 450 °C. Its cation exchange capacity ranged from 191.2 to 208 meq/100 g, depending on activation conditions, and it exhibited a stable zero point of charge at pH 3 (Kandah et al., 2006; Saad et al., 2024; Senila and Cadar, 2024).

Methods and instrumentation

Detergents (ABS and LAS) were quantified by ion-pairing with crystal violet dye and benzene extraction, with spectrophotometric detection at 605 nm or colorimetric detection at 610 nm. Carwash water samples from five stations (Alozi, Total, Almanaseer, Alwataneh, and Alhajawi) were filtered through sand and tested for MBAS adsorption on zeolite and activated carbon. Batch adsorption experiments assessed various adsorbent dosages (0.1–2.0 g), contact times (5–120 min), and temperatures (25, 35, 45 °C) under controlled pH (6.8) and 25 °C conditions. A Jar Testing Apparatus was used, and residual SDBS-MBAS concentrations were measured after shaking and filtering. All tests were conducted in triplicate for accuracy (Shi et al., 2018; Kumar and Maurya, 2022; Tran-Nguyen et al., 2023). Optimization of adsorption focused on balancing efficiency and cost-effectiveness, particularly for locally abundant zeolite.

The optimal conditions for zeolite were identified as 1.0 g dosage and 30 minutes contact time. Activated carbon was prepared at the wastewater lab of Jordan University and tested under identical conditions for comparison.

Performance indicators

Key adsorption metrics, such as uptake efficiency (E), uptake capacity (qe), and partition coefficient (K_d), were calculated using established equations (Agarwal et al., 2021; Kharabsheh and Bdour, 2025). For example:

Uptake efficiency (*E*) evaluates the percentage of SDBS removed from the solution, as described by Equation 1:

$$E = \frac{C_o - C_e}{C_o} \times 100\% \quad (1)$$

where: C_o – the initial concentration of SDBS (mg/L); C_e – the residual concentration of SDBS ion in the solution after equili rium (mg/L).

Uptake capacity (qe) reflects the amount of adsorbate adsorbed per gram of adsorbent Equation 2:

$$q_e = \frac{(C_o - C_e) \times V}{m} \times 100\% \quad (2)$$

where: q_e – the amount of SDBS uptake by synthesized natural zeolite (mg SDBS/g of natural zeolite), V – the volume of the solution (L) and m – the natural zeolite dose (g), m – the weight of zeolite dose (g). Further details can be referenced in (Agarwal et al., 2021; Kharabsheh and Bdour, 2025).

Partition coefficient, K_d (L/g)

$$K_d = \frac{(C_o - C_e) \times V}{C_O \times m} \times 100\% \quad (3)$$

Adsorption isotherms and kinetics: The adsorption behavior was evaluated using Langmuir and Freundlich isotherm models, which describe monolayer and heterogeneous adsorption, respectively. Key equations, such as the linearized Langmuir and Freundlich models, were applied to extract adsorption parameters (e.g., *qm, K_L, K_f, and n*). A detailed comparison of these models is provided in (Ma and Lothenbach, 2020). Adsorption kinetics were analyzed using the pseudo-second-order model, which showed the best fit to experimental data based on (Equation 4).

$$\frac{t}{q_e} = \frac{1}{K_2 (q_c{}^2)} + \frac{t}{q_c} n \quad (4)$$

where: q_e are the adsorption capacity at equilibrium and at time t, respectively (mg/g), K_2 is the rate constant of the three models respectively (min^{-1}), t: the adsorption mixing time in second.

Thermodynamic analysis: The thermodynamic parameters, Gibbs free energy (ΔG◦, kJ/mol), enthalpy (ΔH_o, KJ/mol), and entropy (ΔS, kJ/mol) (J/K/ mol) were determined. The equilibrium constant (K_d) was used to calculate these values (Ma and Lothenbach 2020, Kamal and Abbas 2022).

$$Ln\, K_d = \frac{\Delta S_o}{R} - \frac{\Delta H_o}{RT}, \Delta G_O = \Delta H_O - T\Delta \quad (5)$$

where: T – represent the temperature in Kelvin and R – the gas constant. A graph plot of $ln\ K_d$ against $1/T$ gives a slope of $\Delta H_o/R$ and an intercept of $\Delta S_o/R$, from which ΔS_o and ΔH_o can be determined. The change in Gibbs free energy (ΔG_o, kJ/mol) was calculated as follows: error analysis: model fitting was evaluated using (R^2), mean square error (MSE), and Chi-square (χ^2) tests to ensure robust prediction accuracy. Equations for MSE and (χ^2) are given in (Ma and Lothenbach 2020; Han et al. 2009).

RESULTS AND DISCUSSIONS

The experimental results shown in Table I demonstrate the adsorption efficiency of MBAS on natural zeolite and activated carbon at varying adsorbent doses (0.1 g, 0.5 g, 1.0 g, 1.5 g, and 2.0 g) over different contact times (5 to 120 minutes).

Contact time, dosage, and temperature effects on MBAS (SDBS) adsorption

The adsorption of SDBS-MBAS ions was studied under varying conditions of contact time, adsorbent dose, and temperature to understand their effects on removal efficiency.

Effect of contact time

The time-dependent behavior of SDBS-MBAS ions was studied by varying contact time (5–120 minutes) under optimal conditions. Adsorption efficiency for zeolite rose sharply within the first 30 minutes, reaching 89.47% at a 1.0 g

Table 1. Adsorption efficiency of mbas (%) on natural zeolite and activated carbon at varying doses (0.1 g, 0.5 g, 1.0 g, 1.5 g, and 2.0 g) and contact times (5 to 120 minutes)

Time (min)	Material	Adsorption efficiency of MBAS (%)at varying doses				
		0.1 g (%)	0.5 g (%)	1.0 g (%)	1.5 g (%)	2.0 g (%)
5	Zeolite	74.74	75.79	86.84	89.47	91.58
10	Zeolite	75	76.84	87.37	90	92.11
30	Zeolite	76.32	77.37	89.47	91.58	93.68
50	Zeolite	76.32	77.37	91.58	92.63	94.74
60	Zeolite	78.95	77.89	93.68	94.74	95.79
80	Zeolite	78.47	78.32	92.89	94.74	95.26
100	Zeolite	78.79	78.47	93.68	94.74	95.26
120	Zeolite	78.95	78.47	93.37	94.74	95.79
5	Activated carbon	82.11	57.89	97.63	97.89	98.16
10	Activated carbon	83.16	60.53	97.37	98.16	98.42
30	Activated carbon	96.84	96.05	98.42	98.68	98.95
50	Activated carbon	97.37	96.32	98.68	98.95	99.21
60	Activated carbon	97.79	97.37	98.26	98.53	98.74
80	Activated carbon	97.37	97	98.42	98.68	98.95
100	Activated carbon	97.89	98.11	98.58	98.68	99.05
120	Activated carbon	97.89	98.11	98.58	98.68	99.05

dose. It increased slightly thereafter, achieving equilibrium at 120 minutes with 93.37% uptake, as shown in Figure 1.

Activated carbon showed significantly higher adsorption efficiency, starting at 97.63% within 5 minutes at a 1.0 g dose and reaching near-equilibrium (98.58%) in 30 minutes, remaining stable thereafter. The rapid initial adsorption for both adsorbents indicates quick occupation of active sites, while the slower rate for zeolite after 30 minutes suggests reduced site availability and slower SDBS ion diffusion into micropores. Activated carbon's high initial and consistent efficiency (above 97%) underscores its superior adsorption capacity compared to zeolite under identical conditions. A 30-minute contact time with a 1.0 g dose is sufficient for high removal efficiency in both adsorbents, consistent with studies on SDBS removal using activated carbon from almond husks (Omri, Benzina, and Ammar 2013). Uptake

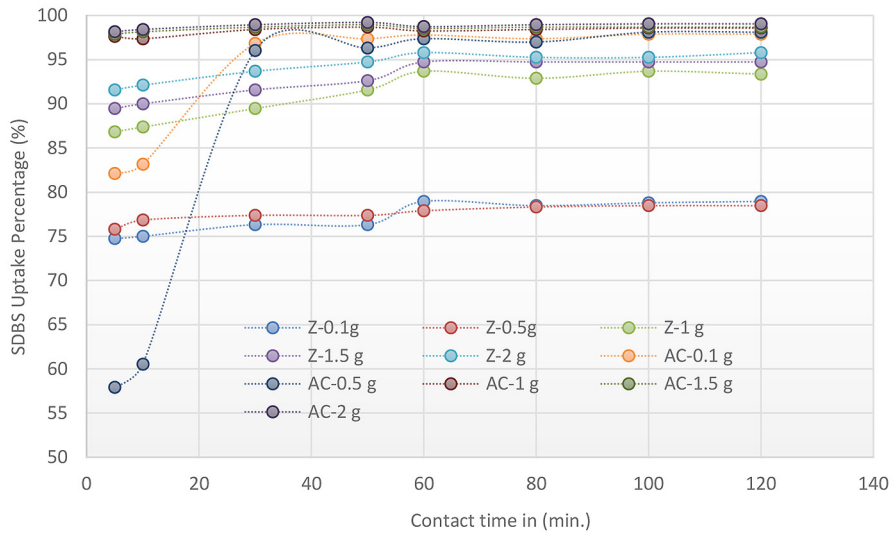

Figure 1. The percentage uptake of SDBS as function of time (5, 30, 50, 60, 80, 100, and 120 minutes) at different adsorbent doses of 0.1 g, 0.5 g, 1.0 g, 1.5 g, and 2.0 g

efficiency also depends on adsorbent properties, operational parameters, and external conditions like temperature and pH (Siswantara et al., 2024).

Effect of adsorbent dose:

The adsorption of SDBS-MBAS was evaluated using varying doses (0.1–2.0 g) of zeolite and activated carbon at pH 6.8, 25 °C, and 30-minute contact time. Zeolite's uptake efficiency improved with dosage and contact time, reaching 93.37% at 1.0 g after 120 minutes and 95.79% at 2.0 g. Activated carbon outperformed zeolite, achieving 98.42% at 1.0 g in 30 minutes, with minimal improvement to 98.58% after 120 minutes. Even at 0.1 g, activated carbon showed high efficiency (96.84% at 30 minutes), peaking at 99.05% with a 2.0 g dose after 120 minutes.

Figure 2 demonstrate that while both zeolite and activated carbon exhibit time-dependent adsorption performance, activated carbon consistently achieves higher uptake efficiencies. The enhanced performance of activated carbon can be attributed to its larger surface area and more effective adsorption sites compared to zeolite. The trend of increased efficiency with higher doses is consistent with findings by Agarwal et al. (2021), who reported that increasing the activated carbon dose from 0.1 g to 1.0 g improved SDBS uptake efficiency significantly, achieving near-complete removal at the highest dose. This suggests that higher adsorbent doses provide more binding sites, thereby enhancing adsorption efficiency (Al-Zboon et al., 2016; Huda et al., 2024).

Table 2 shows that activated carbon consistently outperforms natural zeolite across all doses. Specifically, at a 0.1 g dose, activated carbon achieves an uptake efficiency of 96.84%, whereas natural zeolite achieves 74.74%, resulting in a 22.1% exceedance by activated carbon. At the 0.5 g dose, activated carbon maintains a higher uptake efficiency of 96.05%, while natural zeolite improves slightly to 75.79%, resulting in a 20.26% exceedance. At the highest dose of 1.0 g, activated carbon achieves an uptake efficiency of 98.42%, compared to 89.47% for natural zeolite, reducing the exceedance to 8.95%. These results highlight the superior adsorption capacity of activated carbon, particularly at lower doses, making it a more effective adsorbent for SDBS removal compared to natural zeolite. The diminishing exceedance at higher doses indicates that natural zeolite's performance improves with increased dosage but still does not match the efficiency of activated carbon. These findings are crucial for optimizing the selection and dosage of adsorbents in water and wastewater treatment processes involving MBAS (Ghaderi et al., 2018). Using values shown in Table I, adsorption efficiency was optimized by systematically evaluating the combined effects of adsorbent dosage, contact time, and operational cost. Emphasis

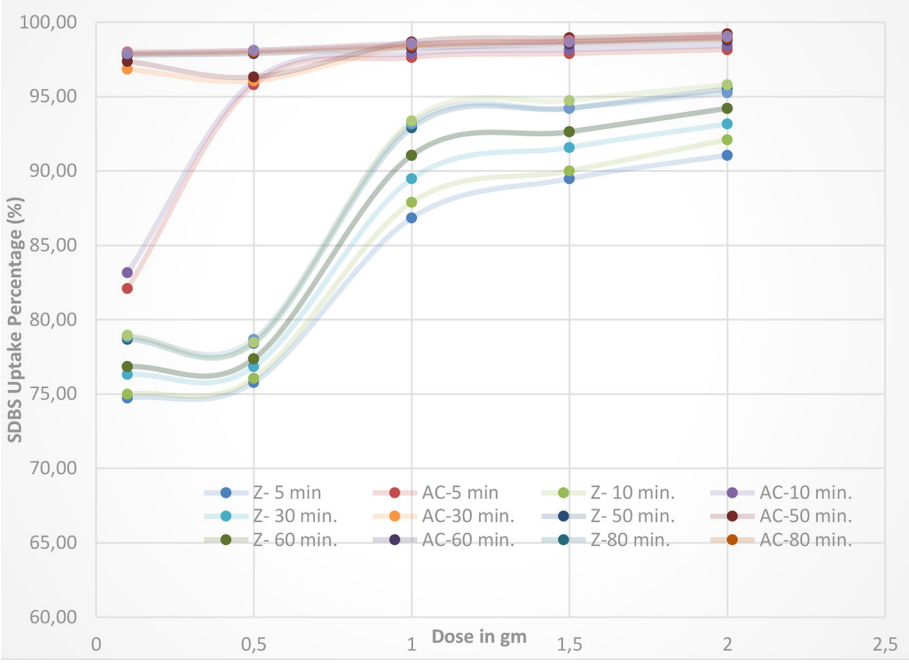

Figure 2. The uptake percentage of SDBS at different adsorbent doses of 0.1 g, 0.5 g, 1.0 g, 1.5 g, and 2.0 g

was placed on balancing high removal efficiency with cost-effectiveness, especially for zeolite, given its local abundance and economic advantage over activated carbon. The optimization results indicated that zeolite achieved its highest removal efficiency (95.79%) at a 2.0 g dosage with a 60-minute contact time. In contrast, activated carbon reached a maximum removal efficiency of 99.21% under optimal conditions of a 2.0 g dosage and a 50-minute contact time. At a lower dosage of 1.0 g, zeolite removed 93.68% of the target substance in 60 minutes, while activated carbon achieved 98.42% removal in just 30 minutes. This analysis identified 1.0 g and 30 minutes as the optimal dosage-time combination for zeolite, balancing high efficiency and practicality. Given its significantly lower cost, zeolite emerged as a more economically viable option, despite its slightly lower removal efficiency compared to activated carbon.

While activated carbon consistently outperformed natural Jordanian zeolite in terms of removal efficiency (99.21% vs. 95.79%), zeolite remains a viable alternative due to its cost-effectiveness, local availability, and environmental advantages. Its slightly lower efficiency can be offset by its affordability and suitability for long-term, cost-sensitive applications, especially in regions with resource constraints. Therefore, Jordanian zeolite is recommended for scenarios where operational costs and sustainability are prioritized over marginally higher removal rates.

Effect of temperature:

Figure 3 illustrates the effect of temperature on the adsorption efficiency of SDBS using natural zeolite and activated carbon. The uptake efficiency increases moderately with temperature, indicative of an endothermic adsorption process. The temperature effect is more significant at higher adsorbent doses, suggesting that increased thermal energy enhances pore availability and ion mobility, thereby improving adsorption.

For a 1 g adsorbent dose, the uptake efficiency of natural zeolite increased from 89.47% at 25 °C to 93.68% at 45 °C, representing a 4.7% improvement. In comparison, the efficiency for activated carbon increased from 98.42% at 25 °C to 98.95% at 45 °C, showing a smaller but noticeable 0.53% increase. These findings suggest that while both adsorbents benefit from higher temperatures, natural zeolite demonstrates a more pronounced temperature dependency. This enhanced adsorption performance of natural zeolite with rising temperature could be attributed to its thermally activated pore expansion and increased binding interactions. These results are consistent with prior studies in the literature, which emphasize the role of temperature in improving

Table 2. Comparison between the uptake percentage of sdbs by natural zeolite and activated carbon (30 minutes)

Adsorbent	% MBAS uptake at				
	0.1 g	0.5 g	1.0 g	1.5 g	2.0 g
Natural zeolite	74.74	75.79	89.47	91.58	93.68
Activated carbon	96.84	96.05	98.42	98.68	98.95
% Exceedance	22.1	20.2	8.95	7.1	5.27

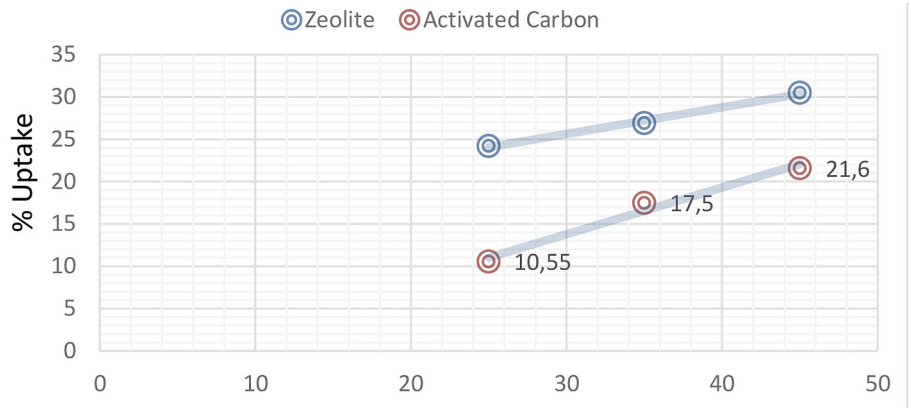

Figure 3. The percentage uptake of SDBS as a function of temperature (25, 35, 45 °C)

adsorption efficiency, particularly for natural adsorbents (Mundim et al., 2023; Özdemir et al. 2011; Taffarel and Rubio 2010).

Thermodynamic analysis:

Thermodynamic parameters (ΔH, ΔS, and ΔG) were calculated for both adsorbents and are shown in Table III. The enthalpy change (ΔH_0) for activated carbon 28.37 kJ/molis significantly higher than for zeolite 9.08 kJ/mol, indicating that the adsorption process with activated carbon requires more energy and involves stronger interactions between the adsorbent and adsorbate. Similarly, the entropy change (ΔS_0) is greater for activated carbon 0.1151 kJ/K/mol compared to zeolite 0.0569 kJ/K/mol. This suggests that the adsorption process with activated carbon leads to greater disorder or randomness, likely due to its more complex structure and surface interactions. The Gibbs free energy change (ΔG_0), which reflects the spontaneity of the adsorption process, is more negative for zeolite at all temperatures (25 °C, 35 °C, and 45 °C). For example, at 25 °C, (ΔG_0) for zeolite is -7.89 kJ/mol, while for activated carbon it is -5.95 kJ/mol. Zeolite exhibits a more favorable and spontaneous adsorption process than activated carbon across all temperatures. The increasingly negative ΔG° with rising temperature indicates enhanced spontaneity for both materials, with zeolite remaining thermodynamically superior. Although activated carbon shows higher enthalpy and entropy changes, reflecting a more energy-intensive and disordered process, zeolite's more negative Gibbs free energy highlights its greater spontaneity, especially at lower temperatures.

Isotherm study

The adsorption of MBAS-SDBS onto zeolite and activated carbon was evaluated using adsorption models (as shown in Table 4 and Table 5). Both followed the Langmuir isotherm, with activated carbon showing higher inverse concentration values, indicating greater affinity for MBAS-SDBS. The Freundlich model further confirmed activated carbon's superior adsorption, reflected by higher log qe and lower log C_e values.

The pseudo-second-order model revealed chemisorption as the dominant mechanism. Activated carbon exhibited a higher qe/Ce ratio, faster kinetics, and greater uptake capacity, achieving equilibrium more quickly than zeolite. While zeolite showed gradual improvement over time, activated carbon's efficiency and speed make it ideal for rapid MBAS-SDBS removal. Zeolite remains a cost-effective option for applications with longer contact times.

Further analysis of the adsorption behavior was conducted using six isotherms to better understand the residual concentration of SDBS in the solution before and after the adsorption process, varying adsorbent dose (zeolite or activated carbon), and mixing time. Table IV presents the results of the R^2, qm, and K_L values for four

Table 3. Calculations for the thermodynamic_

Parameter	Zeolite	Activated carbon
Enthalpy (ΔH_0)	9.08 kJ/mol	28.37 kJ/mol
Entropy change (ΔS_0)	0.0569 kJ/K/mol	0.1151 kJ/K/mol/
ΔG_0@25°C (298.15 K)	-7.89 kJ/mol	-5.95 kJ/mol
ΔG_0@35°C (308.15 K)	-8.46 kJ/mol	-7.10 kJ/mol
ΔG_0@45°C (318.15 K)	-9.03 kJ/mol	-8.25 kJ/mol

Table 4. MBAS-SDBS concentration in (mg/L) at zeolite dose 1.0 g with five mixing time (5, 30, 60,120) minutes

Time of mixing (minute)	Langmuir first order		Langmuir second order		Langmuir third order		Langmuir forth oder		Freundlich isotherm		Pseudo second order
t	Ce	1/Ce	1/Ce	1/qe	qe/Ce	qe	qe	qe/Ce	log Ce	Log qe	t/qe
5	2.5	0.4	0.4	1.21	0.33	0.825	0.825	0.33	0.40	-0.08	6.1
30	2	0.5	0.5	1.17	0.43	0.85	0.85	0.43	0.30	-0.07	23.5
60	1.3	0.77	0.77	1.13	0.69	0.885	0.885	0.69	0.11	-0.05	67.8
120	1.25	0.8	0.8	1.12	0.71	0.8875	0.8875	0.71	0.09	-0.052	135.2

Langmuir models, which were applied first to natural zeolite and then to activated carbon as adsorbents. For natural zeolite, the Langmuir Type 1 model had the best fit with an R^2 value of 0.99, followed by Type 4 (R^2 = 0.96), Type 2 (R^2 = 0.95), and Type 3 (R^2 = 0.94) at pH = 6.8 and temperature = 25 °C. For activated carbon, Langmuir Type 1 had the highest R^2 of 1, indicating an ideal fit, followed by Types 2 and 4 with R^2 values of 0.98 and 0.97, respectively. Taffarel and Rubio (2024) investigated the adsorption efficiency of SDBS from aqueous solutions and found that equilibrium data showed excellent correlation with the Langmuir isotherm model (Taffarel and Rubio 2010). The determination coefficients R^2, values of K_L, K_f, K_2, qm , qc, R^2, and n, were determined from the slope and intercept of the plots in Figure 4.

Freundlich parameters (n and $_{Kf}$) were derived from the slopes and intercepts of linear plots for MBAS-SDBS adsorption on zeolite (at 25°C and pH 6.8). The Freundlich model showed a higher correlation coefficient for zeolite (R^2 = 0.98) than for activated carbon (R^2 = 0.95), indicating a better fit for zeolite under these conditions. However, the Langmuir model demonstrated a higher overall goodness of fit, particularly for activated carbon, suggesting homogenous adsorption on activated carbon and more heterogeneous adsorption on zeolite. The values of n (9.7 for zeolite, 0.02 for activated carbon) suggest favorable adsorption of SDBS on zeolite. Lin (2025) studied surfactant-modified zeolites for tannic acid removal and found that the Freundlich model was less fitting with adsorption data, corroborating our findings. It is a hybrid form of Langmuir and Freundlich equations incorporating a linear relation in the numerator and an exponential function in the denominator (Lin et al. 2011), and therefore can be applied in either homogenous or heterogeneous systems due to its high versatility. The values of K_L, q_m and R^2 were determined by excel solver with minimum error calculation (Table V). The coefficient of correlation values were 0.92,1.0 respectively, for all pH and temperature ranges, which indicates a high fitness of the model with adsorption process. Since the value of R^2

Table 5. MBAS-SDBS concentration in (mg/l) at activated carbon dose=1.0 g with five mixing time (5, 30, 60,120) minutes

Time of mixing (minutes)	Langmuir first order		Langmuir second order		Langmuir third order		Langmuir forth order		Freundlich isotherm		Pseudo second order
t	Ce	1/Ce	1/Ce	1/qe	qe/Ce	qe	0.926	1.93	logCe	log qe	5.40
5	0.48	2.08	2.08	1.08	1.93	0.926	0.928	2.06	0.32	-0.03	21.56
30	0.45	2.22	2.22	1.08	2.06	0.928	0.933	2.66	0.35	-0.03	64.34
60	0.35	2.86	2.86	1.07	2.66	0.933	0.935	3.12	0.46	-0.03	128.34
120	Ce	1/Ce	3.33	1.07	3.12	0.935	0.926	1.93	0.52	-0.03	5.40

Table 6. Adsorption isotherms for SDBS removal by natural zeolite and activated carbon

Natural zeolite														
Langmuir model form (1)					Langmuir model form (2)					Langmuir model form (3)				
R^2	q_m	K_L	MSE	χ^2	R^2	q_m	K_L	MSE	χ^2	R^2	q_m	K_L	MSE	χ^2
0.99	0.77	5.89	0.009	0.012	0.95	0.78	6.25	0.007	0.009	0.94	0.81	6.40	0.003	0.004
Langmuir model form (4)					Freundlich isotherm					Pseudo-second-order model				
R^2	q_m	K_L	MSE	χ^2	R^2	n	K_f	MSE	χ^2	R^2	q_c	K_2	MSE	χ^2
0.96	2.2	0.10	1.84	0.83	0.98	9.69	0.96	0.01	0.001	0.92	0.03	28.6	0.69	23.1
Activated carbon														
Langmuir model form (1)					Langmuir model form (2)					Langmuir model form (3)				
R^2	q_m	K_L	MSE	χ^2	R^2	q_m	K_L	MSE	χ^2	R^2	q_m	K_L	MSE	χ^2
1	0.91	5.00	0.0004	0.0005	0.98	0.93	130.4	10^{-5}	10^{-5}	0.98	0.91	133.3	0.0004	0.0005
Langmuir model form (4)					Freundlich isotherm					Pseudo-second-order model				
R^2	q_m	K_L	MSE	χ^2	R^2	n	K_f	MSE	χ^2	R^2	q_c	K_2	MSE	χ^2
0.97	0.91	131	0.0004	0.0005	0.95	0.02	1.096	0.0004	0.0004	1	0.94	6.184	0.0003	0.0004

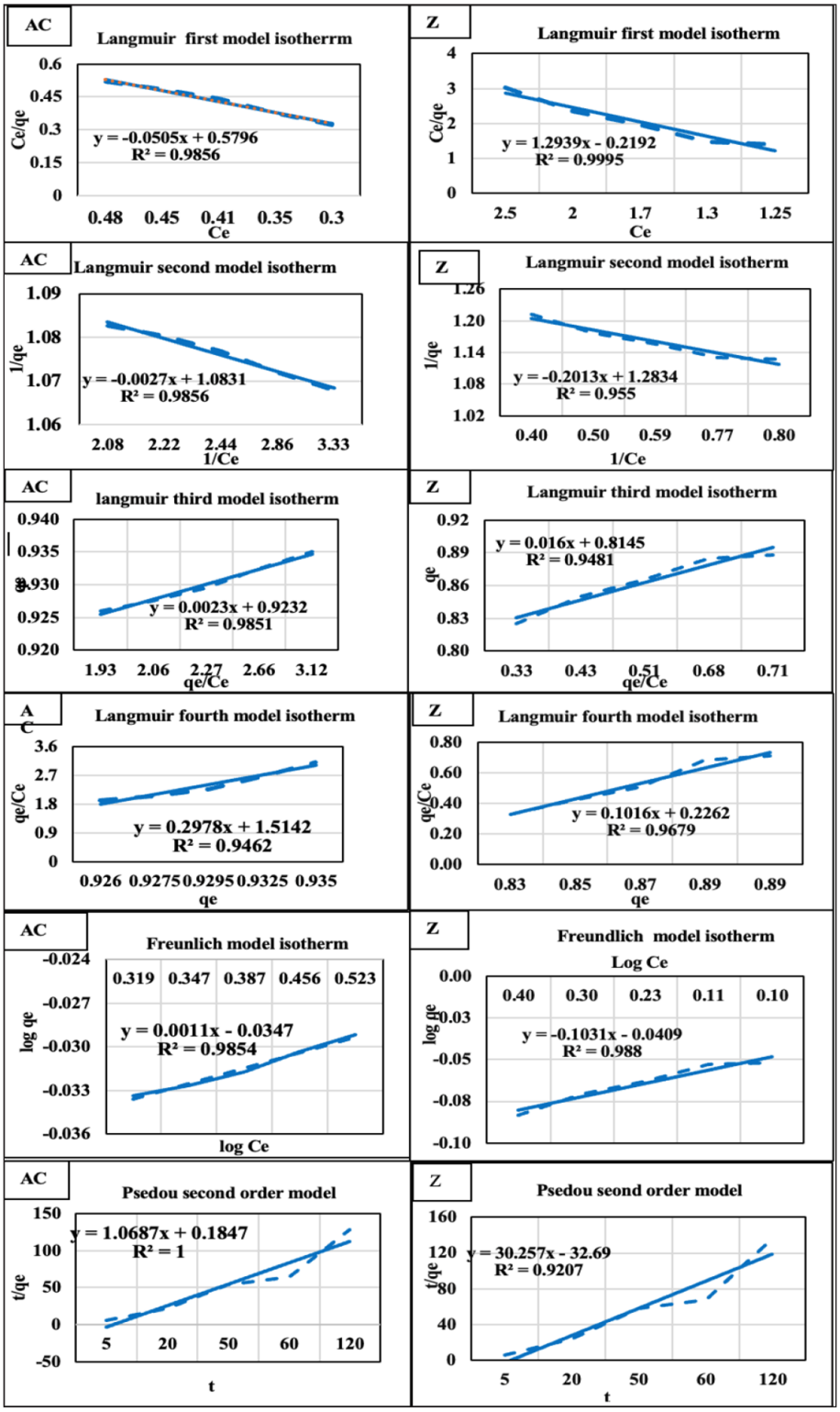

Figure 4. Zeolite and activated carbon adsorption isotherms of SDBS-MBAS with linear equations and coefficient of determination R^2

is equal to 1 in the case of using activated carbon as adsorbent, this indicates that the adsorption system is homogenous which supported Langmuir assumption. Zhou et al. (2022) found that adsorption of SDBS on nano ZIF-8 well fitted the pseudo-second order kinetic model and Langmuir adsorption model. This suggests that the adsorption process was more homogeneous in the case of activated carbon, as supported by the Langmuir assumption. Error metrics analysis – Mean

Squared Error (MSE) and Chi-Square (χ^2) were used to evaluate the accuracy of predicted Ce/q values for the Langmuir type 1, Freundlich, and Pseudo-second-order models. As shown in Table II, the Freundlich model had the lowest MSE and χ^2 values for natural zeolite, followed by Langmuir type 3, while the Pseudo-second-order model exhibited the highest errors. For activated carbon, Langmuir type 2 demonstrated the highest accuracy, with the lowest error values, while other isotherm models had relatively similar error magnitudes. These findings validate the Freundlich and Langmuir models in describing the adsorption process.

CONCLUSIONS

This study investigated the suitability of natural zeolite and activated carbon for the removal of SDBS-MBAS from raw carwash wastewater. The characterization of volcanic tuff and geopolymer provided valuable insights into the adsorbent properties. Isotherm and kinetic studies revealed that natural zeolite achieved a maximum removal efficiency of 95.79% at a dosage of 2.0 g and a contact time of 60 minutes, while activated carbon reached a maximum efficiency of 99.21% under similar conditions (2.0 g dosage and 50-minute contact time). Both adsorbents exhibited optimal removal at pH 6.8, with an optimal dosage of 1.0 g and a feasible contact time of 30 minutes. Natural zeolite demonstrated good potential for SDBS-MBAS removal, achieving 93.68% removal at 1.0 g and 30 minutes. However, activated carbon proved more efficient, particularly for applications requiring rapid adsorption. Thermodynamic analysis indicated that zeolite had a more favorable Gibbs free energy ($\Delta G°$) profile compared to activated carbon, suggesting a more spontaneous adsorption process. The enthalpy ($\Delta H°$) and entropy ($\Delta S°$) changes for activated carbon were higher, indicating a more energy-intensive and disorderly process.

The adsorption behavior of MBAS-SDBS onto both adsorbents was analyzed using Langmuir and Freundlich isotherms. Both adsorbents followed the Langmuir isotherm, indicating monolayer adsorption on a surface with finite adsorption sites. Activated carbon demonstrated a higher adsorption capacity, reflected by lower equilibrium concentrations and higher uptake capacities. The Freundlich isotherm suggested that activated carbon had a more favorable adsorption profile due to its heterogeneous adsorption sites. In comparison, zeolite showed steady improvement in adsorption over time, but activated carbon consistently exhibited superior efficiency and faster kinetics. This highlight activated carbon's suitability for applications requiring rapid MBAS-SDBS removal, although zeolite remains a viable option when cost or longer contact times are considered. The adsorption process for both adsorbents was endothermic, spontaneous, and irreversible. The isotherm study showed that natural zeolite fit both the Langmuir and Freundlich models well, while the Pseudo-second-order model showed the highest error values. For activated carbon, the Langmuir and Pseudo-second-order models provided the best fit. The maximum uptake capacity of SDBS using natural zeolite, as predicted by the Langmuir model, increased from 24% to 31% as the temperature increased from 25°C to 45°C, while for activated carbon, the uptake capacity increased from 11% to 22%. Based on these results, natural volcanic tuff, though slightly less efficient than activated carbon, can be considered a cost-effective alternative for SDBS removal, especially in long-term, cost-sensitive applications.

Acknowledgment

The authors would like to express their gratitude for the support extended to them throughout this research project by the colleagues and staff of Jordan University.

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