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INVESTIGATION OF ISOTHERMAL REGULARITIES OF THE ADSORPTION PROCESS IN COMPOSITE SORBENTS

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Abstract

This study investigates the isothermal regularities of the adsorption process in composite sorbents. Composite materials prepared from peanut shells and Ailanthus wood sawdust were used as sorbents. The efficiency of the adsorption process was evaluated based on experimental data obtained at different initial concentrations by determining the equilibrium concentration and sorption capacity. The Langmuir and Freundlich isotherm models were applied for the theoretical description of the adsorption process. The obtained results demonstrated that the sorption capacity increases with increasing initial adsorbate concentration and tends toward equilibrium at higher concentrations. The analysis revealed that the YAD:KOH–10 sorbent exhibited the highest adsorption capacity, with a maximum value of 23.24 mg/g. The high correlation coefficient values obtained using the Langmuir model (R^2 = 0.988–0.997) indicate that the adsorption process mainly proceeds through a monolayer adsorption mechanism. The values of the parameter n>1 in the Freundlich model confirm the thermodynamic favorability of the adsorption process. The obtained results demonstrate the high efficiency of the composite sorbents and their potential application as promising adsorbents for the purification of wastewater contaminated with petroleum products.

Keywords: *composite, sorbent, lignocellulose, sorption, Langmuir model, Freundlich model, adsorption isotherms*

Introduction

At present, the rapid development of the oil and gas, chemical, and energy industries has led to increasing contamination of water resources by organic and inorganic pollutants, making environmental protection one of the major global challenges (Foo & Hameed, 2020; Saka & Balbay, 2021). In particular, wastewater contaminated with petroleum products negatively affects aquatic ecosystems and human health (Adegoke et al., 2021; Li et al., 2022). Therefore, the development of efficient wastewater treatment technologies and environmentally safe adsorbent materials is of significant scientific and practical importance (Ahmed & Hameed, 2023; Wang et al., 2023). Among water purification methods, adsorption is distinguished by its high efficiency, economic feasibility, and technological simplicity (Foo & Hameed, 2020; Rahman et al., 2022). The efficiency of adsorption largely depends on the specific surface area, porous structure, and active adsorption sites of the sorbent material (Islam et al., 2021; Zhang et al., 2022). In this regard, composite sorbents have attracted considerable attention. In particular, lignocellulosic raw materials such as peanut shells and wood sawdust are considered promising precursors for adsorbent production due to their low cost, renewability, and environmental safety (Islam et al., 2021; Kumar et al., 2023; Chen et al., 2024). Chemical activation significantly improves their adsorption properties by enhancing pore structure and surface activity (Li et al., 2022; Kumar et al., 2023; Singh et al., 2025). The Langmuir and Freundlich isotherm models are widely used for the theoretical analysis of adsorption processes (Foo, K.Y., & Hameed, B.H., 2020; Rahman, M. M., & others., 2022; Ahmed, M.J., & Hameed, B.H., 2023). The Langmuir model describes monolayer adsorption on homogeneous surfaces, whereas the Freundlich model characterizes multilayer adsorption on heterogeneous surfaces (Rahman et al., 2022; Ahmed & Hameed, 2023). These models make it possible to determine the adsorption mechanism and the maximum adsorption capacity of sorbents (Foo, K.Y., & Hameed, B.H., 2020; Ahmed, M.J., & Hameed, B.H., 2023). The aim of this study is to investigate the isothermal regularities of the adsorption process in composite sorbents prepared from peanut shells and Ailanthus wood sawdust and to evaluate their adsorption efficiency based on the Langmuir and Freundlich models. In contrast to conventional single-component adsorbents, the composite sorbents developed in this study combine peanut shell biomass and Ailanthus wood sawdust, resulting in a synergistic effect that enhances adsorption performance. The interaction between the lignocellulosic matrices of the two components and KOH chemical activation contributed to the development of a highly porous carbon structure with an increased number of active adsorption sites (Kumar, A., & others., 2023; Singh, P., & others., 2025). In particular, the YAD:-KOH–10 composite sorbent demonstrated superior adsorption efficiency, which may be attributed to the improved pore development, enhanced surface heterogeneity, and favorable distribution of functional groups formed during pyrolysis and activation (Zhang et al., 2022; Chen et al., 2024; Zhou et al., 2025). Therefore, the prepared composite sorbents represent promising low-cost adsorbent materials for wastewater purification from petroleum contaminants.

Materials and Methods

In this study, composite materials prepared from peanut shells and Ailanthus wood sawdust were used as sorbents. The raw materials were initially cleaned from mechanical impurities and dust particles and then washed with distilled water. The washed samples were dried at 105 °C for 4–6 h. The dried materials were crushed, sieved to obtain a particle size fraction of 1–3 mm, and mixed at a mass ratio of 25:75 for peanut shells and Ailanthus wood sawdust, respectively. To improve the adsorption properties, the obtained raw materials were chemically activated using 5–10 % potassium hydroxide (KOH) solutions. The activation process was carried out at 40–60 °C for 2–4 h. Depending on the composition and reagent concentration, the treated samples were conditionally designated as follows: samples based on peanut shells - YP:KOH-5, YP:KOH-6, YP:-KOH-7, YP:KOH-8, YP:KOH-9, YP:KOH-10; samples based on Ailanthus wood sawdust - AD:KOH-5, AD:KOH-6, AD:KOH-7, AD:-KOH-8, AD:KOH-9, AD:KOH-10; composite samples based on peanut shells and Ailanthus wood sawdust - YAD:KOH-5, YAD:-KOH-6, YAD:KOH-7, YAD:KOH-8, YAD:-KOH-9, and YAD:KOH-10. The prepared samples were subjected to pyrolysis and activation in an inert argon (Ar) atmosphere at temperatures ranging from 350 to 700 °C for 60–120 min. As a result of thermal treatment, microporous composite sorbents with a high carbon content were obtained. The activated samples were repeatedly washed with distilled water until a pH value of 6.5–7.0 was achieved in order to remove residual chemical reagents, after which they were dried again at 105 °C. Adsorption experiments were carried out under static conditions using the batch adsorption method at laboratory temperature (25 ± 2 °C). Petroleum products were used as adsorbates. During the experiments, a certain amount of sorbent was added to a solution of a specified volume with different initial concentrations, and the mixture was stirred until adsorption equilibrium was reached. After equilibrium was established, the solutions were filtered and the residual adsorbate concentration was determined. For the theoretical analysis of the adsorption process, the Langmuir and Freundlich isotherm models were applied. The linear form of the Langmuir model ($C_e/q_e - C_e$) and the logarithmic form of the Freundlich model ($\ln q_e - \ln C_e$) were used. Adsorption parameters (q_{max}, K_L, K_F, and n) were determined by regression analysis, and the agreement between the models and experimental data was evaluated using the correlation coefficient (R^2).

Results and Discussion

Based on experimental studies carried out at different initial concentrations, the adsorption isotherms of the composite sorbents were investigated, and the main parameters of equilibrium concentration and sorption capacity were determined.

Table 1. *Adsorption isotherm parameters of composite sorbents at different initial concentrations*

C_0 (mg/L)	C_e (mg/L) YAD:KOH–10	q_e (mg/g) YAD:KOH–10	C_e (mg/L) AD:KOH–10	q_e (mg/g) AD:KOH–10	C_e (mg/L) YP:KOH–10	q_e (mg/g) YP:KOH–10
50	8	4.2	12	3.6	15	3.2
100	18	8.2	25	6.9	30	6.4
150	35	11.5	45	9.6	52	8.8
200	60	14.0	72	11.7	80	10.8
250	90	16.0	105	13.3	115	12.3
300	125	17.8	145	14.8	160	13.8
350	165	19.4	185	16.2	205	15.0

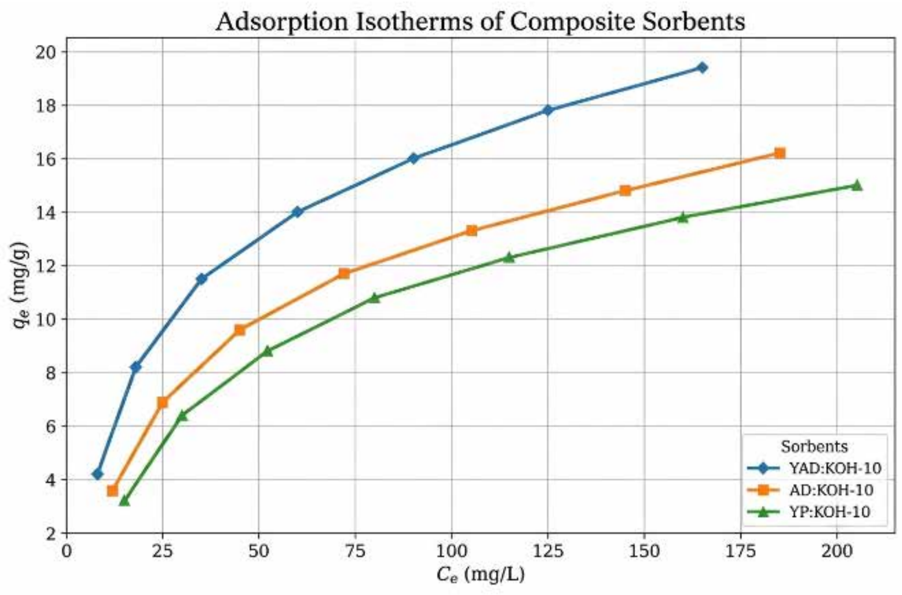
The results presented in the table show that the sorption capacity of all sorbents increased with increasing initial concentration. This indicates an intensive adsorption process due to the presence of active adsorption sites on the sorbent surface.

The highest sorption capacity was observed for the YAD:KOH–10 sorbent, with a maximum value of 19.4 mg/g. For the AD:KOH–10 and YP:KOH–10 sorbents, the corresponding values were 16.2 mg/g and 15.0 mg/g, respectively.

The graph demonstrates that the adsorption capacity increases with increasing concentration; however, at higher concentrations, the process gradually slows down and approaches equilibrium. This behavior can be explained by the gradual saturation of active adsorption sites on the sorbent surface. The analysis of the graph showed that the adsorption efficiency decreases in the following order:

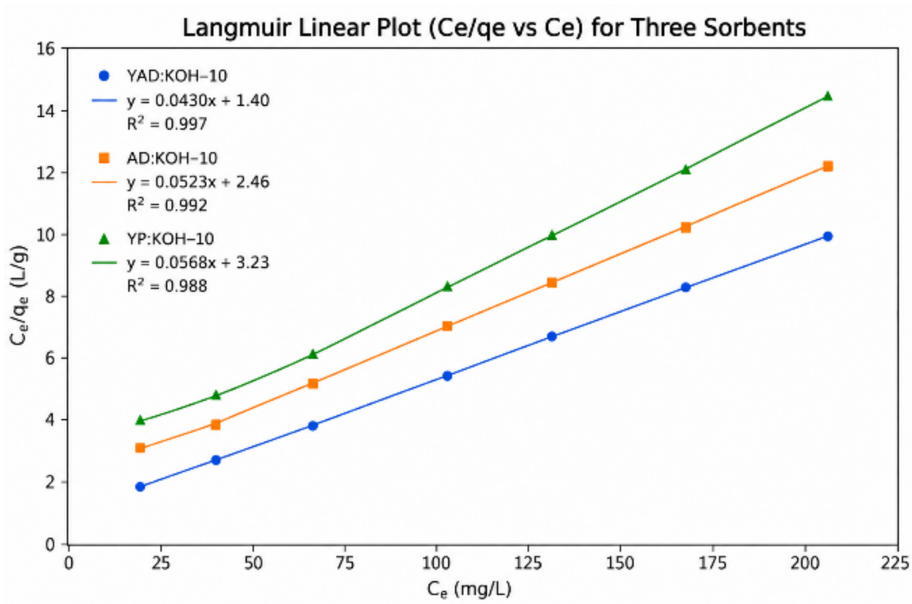
$$\boldsymbol{YAD} : \boldsymbol{KOH} - 10 > \boldsymbol{AD} : \boldsymbol{KOH} - 10 > \boldsymbol{YP} : \boldsymbol{KOH} - 10$$

Figure 1. *Adsorption isotherms of composite sorbents (C_e–q_e)*



In addition, studies were carried out to evaluate the conformity of the composite sorbent samples to the Langmuir isotherm model. The Langmuir model assumes that the adsorption process occurs on energetically homogeneous active sites of the sorbent surface and proceeds through a monolayer adsorption mechanism. The obtained results are presented in Figure 2.

Figure 2. *Linear form of the Langmuir isotherm (C_e/q_e – C_e)*



The experimental data demonstrated a high linear correlation for all sorbents in accordance with the Langmuir isotherm model. The YAD:KOH–10 sorbent exhibited the highest C_e/q_e value, reaching approximately 8.7 L/g at C_e = 200 mg/L, whereas the corresponding values for AD:KOH–10 and YP:KOH–10 were 11.5 and 13.8 L/g, respectively. The high degree of linearity confirms that the adsorption process predominantly follows a monolayer adsorption mechanism.

These findings are further confirmed by the data presented in Table 2, which summarizes the calculated Langmuir isotherm parameters.

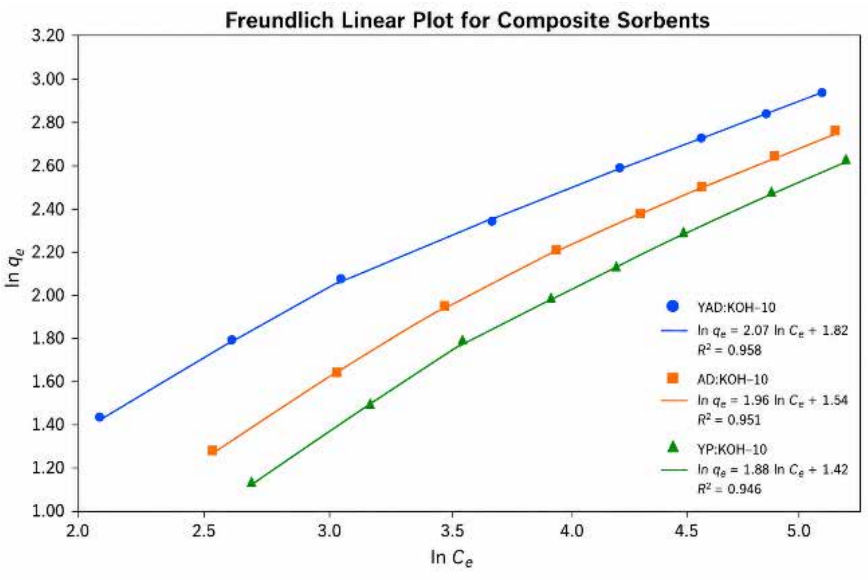
Table 2. *Langmuir model parameters for composite sorbents*

Sorbents	q_{max}(mg/g)	K_L	R^2
YAD:KOH–10	23.24	0.027	0.997
AD:KOH–10	19.10	0.021	0.992
YP:KOH–10	17.60	0.019	0.988

As can be seen from the results, the YAD:KOH−10 sorbent exhibited the highest maximum adsorption capacity, indicating a well-developed porous structure. The high correlation coefficient values obtained for the Langmuir model (R^2 = 0.988–0.997) confirm the strong agreement between the experimental data and the model. This indicates that the adsorption process predominantly proceeds according to a monolayer adsorption mechanism.

In addition, the conformity of the composite sorbents to the Freundlich isotherm model was also investigated. The Freundlich model describes adsorption occurring on energetically heterogeneous and non-uniform surfaces and is widely used to characterize multilayer adsorption processes. This model takes into account the energetically different distribution of active adsorption sites on the sorbent surface. The experimental results obtained based on the Freundlich isotherm model are presented in Figure 3.

Figure 3. *Freundlich plot (lnq_e – lnC_e)*



The Freundlich plot demonstrated a positive correlation between lnq_e and lnC_e for all investigated sorbents, confirming that the adsorption process occurs on energetically heterogeneous surfaces. The YAD:KOH−10 sorbent exhibited the highest adsorption performance, reaching a lnq_e value of approximately 3.0 at lnC_e≈5.2, whereas the corresponding values for AD:KOH−10 and YP:KOH−10 were about 2.8 and 2.7, respectively. The graphical results indicate that the adsorption process is thermodynamically favorable for all sorbents and that the active adsorption sites are energetically non-uniformly distributed over the sorbent surface.

These findings are further confirmed by the data presented in Table 3, which summarizes the calculated Freundlich isotherm model parameters.

The values of n > 1 indicate the favorable nature of the adsorption process. This confirms that the adsorption process for all inve[stigated sorbents is thermodynamically favorable.

A comparison of the correlation coefficients for the Langmuir and Freundlich models showed that the Langmuir model has higher R^2 values. This indicates that adsorption predominantly occurs on energetically homogeneous sorbent surfaces.

Table 3. *Freundlich model parameters*

Sorbents	K_F	n	R^2
YAD:KOH–10	1.82	2.07	0.958
AD:KOH–10	1.54	1.96	0.951
YP:KOH–10	1.42	1.88	0.946

Conclusion

The conducted studies demonstrated that composite sorbents prepared from peanut shells and Ailanthus wood sawdust possess high adsorption activity toward petroleum products. The experimental results showed that the sorption capacity of all investigated sorbents increased with increasing initial concentration. Among the studied sorbents, the YAD:KOH–10 sample exhibited the highest adsorption efficiency. The maximum adsorption capacity calculated using the Langmuir model reached 23.24 mg/g for YAD:KOH–10, while the values for AD:KOH–10 and YP:KOH–10 were 19.10 mg/g and 17.60 mg/g, respectively. The high correlation coefficients obtained for the Langmuir model (R^2 = 0.988–0.997) confirmed the strong agreement between the experimental data and the model, indicating that the adsorption process mainly proceeds through a monolayer adsorption mechanism. The values of $n>1$ obtained from the Freundlich model indicated the thermodynamic favorability of the adsorption process.

The obtained results confirm that KOH-activated composite sorbents possess a well-developed microporous structure and high sorption properties. Therefore, these sorbents can be considered promising adsorbent materials for the effective purification of wastewater contaminated with petroleum products.

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