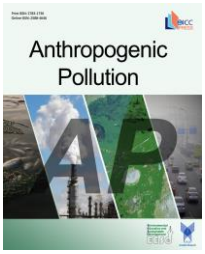

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Research Article

Optimal Adsorption for High COD Reduction in Petrochemical Wastewater Using Pomegranate Peel–Silica Composites

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Abstract

Petrochemical industrial wastewater poses a significant environmental threat due to its high chemical oxygen demand (COD) and diverse pollutants, necessitating sustainable treatment solutions. Despite advances in adsorption, optimal conditions and mechanisms for multi-pollutant removal using composite adsorbents remain underexplored. This study evaluates the efficacy of pomegranate peel and silica-based adsorbents, in simple and composite forms with activated carbon, for removing COD, nitrate, sulfide, turbidity, total dissolved solids (TDS), total suspended solids (TSS), lead (Pb), and zinc (Zn) from PIW. Batch experiments tested organic, inorganic, and composite adsorbents at dosages of 2 and 4 g/L and contact times of 20, 40, and 60 minutes, with three repetitions. The composite adsorbent at 4 g/L and 60 minutes reduced COD by 62.0%, sulfide by 52.7%, Pb by 46.0%, and Zn by 39.8% across initial concentrations of 800–1200 mg/L, outperforming simple adsorbents. Pseudo-first-order kinetics ($R^2 = 0.98$, $\chi^2 = 0.02$) and the Freundlich isotherm ($R^2 = 0.95$) models confirmed physical adsorption via van der Waals forces and multilayer binding. These findings position pomegranate peel–silica composites as effective, scalable solutions for mitigating PIW pollution through optimized multi-pollutant adsorption.

Keywords: Petrochemical wastewater; Adsorption; Pomegranate peel; Silica composite; COD removal

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Highlights

Composite adsorbent achieves 62% COD reduction in petrochemical wastewater at 4 g/L.
Pseudo-first-order kinetics (R^2 = 0.98) drive rapid COD removal in 60 minutes.
Freundlich isotherm (R^2 = 0.95) confirms multilayer adsorption on diverse sites.
Pomegranate peel–silica composite outperforms simple adsorbents for multi-pollutant removal.
Physical adsorption mechanisms enhance scalable PIW treatment strategies.

1. Introduction

Petrochemical industrial wastewater (PIW) represents a critical environmental challenge due to its complex mixture of organic and inorganic pollutants, which threaten aquatic ecosystems, water quality, and human health. These effluents frequently contain not only refractory organics but also heavy metals from catalysts, piping, and raw materials. The presence of high chemical oxygen demand (COD), heavy metals such as lead (Pb) and zinc (Zn), and other contaminants like nitrate, sulfide, total dissolved solids (TDS), and total suspended solids (TSS) in PIW contributes to severe ecological degradation and public health risks (Wei et al 2019). COD measures the amount of oxygen required to chemically oxidize organic and inorganic matter in water, and its removal is a primary goal of wastewater treatment to reduce toxicity and environmental impact. The high COD levels, indicative of organic pollutants, are particularly problematic because they persist in the environment, exert toxicity to aquatic life, and complicate downstream treatment processes.

Adsorption has emerged as a leading physicochemical method for wastewater treatment, valued for its simplicity, cost-effectiveness, and low secondary pollution (Rashid et al 2021). Unlike biological treatments, which are sensitive to temperature fluctuations and require extended processing times, adsorption offers rapid pollutant removal with straightforward operational control (Fawzy et al., 2019). Liu et al. (2021) highlighted adsorption's technical feasibility, environmental safety, and energy efficiency, noting that it requires minimal chemical inputs and produces less sludge compared to methods like chemical precipitation or coagulation (Shi et al., 2019). The choice of adsorbent is pivotal to adsorption's success, with effective materials needing to be abundant, inexpensive, and environmentally benign to ensure scalability and sustainability (Sharma and Singh, 2020).

Previous research has explored a variety of adsorbents for PIW treatment, including agricultural byproducts, biocomposites, and inorganic materials. Pomegranate peel, rich in functional organic groups, has shown significant potential for removing heavy metals and organic pollutants due to its high surface area and binding capacity (Al-Badaii et al., 2024). Similarly, silica-based adsorbents, with their nanoscale porosity, enhance pollutant capture through physical adsorption mechanisms (Venezia et al., 2020). This aligns with the growing application of green-synthesized metal oxide nanoparticles in advanced oxidation processes for degrading complex organic pollutants in industrial wastewaters, as demonstrated for textile effluents and phenolic compounds (Fekri et al., 2021; Nouri-Mashiran et al., 2022). While such catalytic processes target molecular degradation, the focus of this study is on the adsorptive removal of a broad pollutant suite using a silica- and biochar-based composite.

Biocomposites, combining organic and inorganic components, have also demonstrated synergistic effects that improve removal efficiency across diverse pollutants. For instance, Abdel-Aziz et al. (2019) reported that carbon/lignin biocomposites effectively remove aromatic hydrocarbons, such as benzene, toluene, and xylene, from wastewater, leveraging the combined strengths of organic and inorganic matrices. Moreover, Niknejad et al. (2021) showed that high-surface-area biocomposites promote weak, reversible interactions with organic pollutants, thereby facilitating efficient adsorption . Wang et al. (2022) demonstrated rapid heavy metal uptake on modified fruit peels, achieving equilibrium within minutes, which suggests potential for fast-acting adsorbents in PIW treatment.

Despite these advancements, several knowledge gaps persist in the application of adsorption for PIW treatment. First, while individual adsorbents like pomegranate peel or silica have been studied, there is limited research systematically comparing their performance in simple versus composite forms, particularly for multi-pollutant removal in complex wastewater matrices. Al-Badaii et al. (2024) noted site heterogeneity in pomegranate peel adsorbents for boron removal, but their applicability to COD reduction in PIW remains underexplored. Second, the optimization of operational parameters, such as adsorbent dosage and contact time, has not been thoroughly investigated for composite adsorbents, leaving uncertainty about the conditions that maximize pollutant removal efficiency (Sharma and Singh, 2020). Third, the mechanisms governing multi-pollutant removal, particularly the interplay of physical adsorption, kinetic behavior, and surface heterogeneity in composite systems, are not well understood. Wang et al. (2022) focused on heavy metal kinetics but did not address COD-specific mechanisms, a critical gap given COD's prominence in

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PIW. Finally, the scalability of adsorption-based systems for industrial applications remains a challenge, as most studies are confined to laboratory-scale experiments without addressing practical implementation barriers (Fawzy et al., 2019).

This study addresses these gaps by investigating the efficacy of pomegranate peel and silica-based adsorbents for PIW treatment. Both simple and composite forms with activated carbon were evaluated. Their removal efficiency was assessed for multiple pollutants, including COD, nitrate, sulfide, turbidity, TDS, TSS, Pb, and Zn. The use of composite adsorbents is justified by their potential to combine the organic binding capabilities of pomegranate peel with the structural advantages of silica, offering enhanced surface area and adsorption capacity. By systematically evaluating multiple adsorbent types (organic, inorganic, composite), dosages (2 and 4 g/L), and contact times (20, 40, and 60 minutes), this study provides a comprehensive analysis of optimal conditions for multi-pollutant removal. Furthermore, it elucidates the physical adsorption mechanisms and kinetic profiles driving COD reduction, addressing the lack of mechanistic clarity in composite systems. This approach is novel because it integrates the synergistic potential of composite materials with a focus on operational optimization and mechanistic insights, directly targeting the identified gaps in scalability and multi-pollutant treatment.

The primary aim of this study is to evaluate the efficiency of organic, inorganic, and composite adsorbents in removing chemical and physical pollutants from PIW, with an emphasis on achieving maximum COD reduction. The novelty of this work lies in its integrated approach, which systematically compares simple and composite agro-industrial adsorbents for the simultaneous removal of a broad suite of organic, inorganic, and particulate pollutants from real, complex petrochemical wastewater—a scenario not thoroughly addressed in prior research. This study specifically targets the identified gaps concerning composite adsorbent performance, operational optimization, and mechanistic clarity in multi-pollutant matrices. The specific objectives are to: (1) assess the impact of adsorbent type, dosage, and contact time on the removal of COD, nitrate, sulfide, turbidity, TDS, TSS, Pb, and Zn; (2) identify optimal operational conditions for composite adsorbents to achieve robust pollutant removal; and (3) clarify the physical adsorption mechanisms and kinetic profiles governing COD removal. These objectives directly address the identified knowledge gaps by providing a systematic comparison of adsorbent performance, optimizing operational parameters, and elucidating mechanisms for multi-pollutant removal.

2. Material and Methods

2.1. Material

In this study, various materials and instruments were employed to evaluate the reduction of physicochemical pollutants in petrochemical wastewater. Pomegranate peel, sourced locally from agricultural waste, was used as the organic adsorbent due to its abundance, low cost, and high content of functional groups such as hydroxyl and carboxyl groups, which facilitate pollutant binding (Nemr, 2009). The peels were collected from fresh pomegranates, thoroughly washed to remove impurities, and air-dried to ensure consistency.

Nano-silica, selected for its high surface area and adsorption capacity, was used as the inorganic adsorbent (Sigma-Aldrich, particle size <50 nm). Other chemicals included sodium hydroxide (NaOH, 98% purity), sulfuric acid (H_2SO_4, 98%), distilled water, sodium thiosulfate ($Na_2S_2O_3$), iodine solution, hydrochloric acid (HCl, 6N), and starch solution, all of analytical grade (Merck, Germany). Analytical instruments included a UV-Vis spectrophotometer (Hach DR6000) for nitrate and chemical oxygen demand (COD) measurements, a turbidity meter (Hach 2100Q) for turbidity analysis, and a precision balance (Sartorius, 0.1 mg accuracy, Sartorius AG, Germany) for weighing adsorbents and residues. Porcelain capsules and desiccators were used for total dissolved solids (TDS) testing. A pH meter (Metrohm 827) was used to monitor and adjust solution pH, and a scanning electron microscope (SEM, Zeiss Sigma 300) was employed to characterize adsorbent morphology. All experiments were conducted using wastewater samples collected from the Isfahan Petrochemical Complex, Iran, stored at 4°C in polyethylene containers to preserve sample integrity. Wastewater was collected from the Isfahan Petrochemical Complex, Iran. To ensure reproducibility, the initial physicochemical characteristics of the wastewater were analyzed, including COD (800–1200 mg/L), nitrate (50–80 mg/L), sulfide (20–40 mg/L), turbidity (100–150 NTU), TDS (1000–1500 mg/L), total suspended solids (TSS, 200–300 mg/L), lead (Pb, 0.5–1.0 mg/L), and zinc (Zn, 0.8–1.5 mg/L).

2.2. Methods

2.2.1. *Adsorbent Preparation*

To prepare the organic adsorbent, 500 g of dry pomegranate peel powder was mixed with 1 L of sulfuric acid (1 M) under a fume hood and left at room temperature

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(25 ± 2°C) for 24 hours for chemical activation to enhance porosity. Subsequently, 4 L of distilled water was added to terminate the reaction, and the resulting charcoal was filtered using Whatman No. 1 filter paper. A sodium hydroxide solution (0.1 M) was used to neutralize residual acid until the pH reached 6.0 ± 0.2. The activated carbon was washed repeatedly with distilled water to remove impurities, dried in an oven at 105°C for 48 hours, and stored in an airtight glass container (Nemr, 2009). The particle size of the resulting activated carbon was sieved to 100–200 µm to ensure uniformity, and its surface area was determined using Brunauer-Emmett-Teller (BET) analysis (Micromeritics ASAP 2020, surface area: 350 ± 20 m²/g). Nano-silica was used as the inorganic adsorbent without further modification. For the composite adsorbent, organic (pomegranate peel-derived activated carbon) and inorganic (nano-silica) adsorbents were combined in a 1:1 mass ratio, as optimized in preliminary experiments (Khader et al., 2021; Robles-Jimarez et al., 2022). The composite was prepared by mechanically mixing the two adsorbents in distilled water (1 L) under continuous stirring at 200 rpm for 2 hours, followed by filtration and drying at 80°C for 24 hours. The composite was characterized using Fourier-transform infrared spectroscopy (FTIR, PerkinElmer Spectrum 100) to identify functional groups responsible for adsorption.

2.2.2. *Wastewater Treatment Experiments*

The wastewater treatment experiments were conducted in batch mode using 300 mL of petrochemical wastewater per trial. The wastewater was mixed with either the organic adsorbent (pomegranate peel-derived activated carbon), inorganic adsorbent (nano-silica), or composite adsorbent at concentrations of 2 or 4 g/L. Preliminary experiments confirmed these concentrations as optimal for balancing adsorption efficiency and cost. The mixtures were stirred at 150 rpm using a magnetic stirrer (IKA C-MAG HS 7) at room temperature (25 ± 2°C) for contact times of 20, 40, or 60 minutes. Each experiment was performed in triplicate to ensure statistical reliability. Control experiments without adsorbents were conducted under identical conditions to quantify baseline pollutant levels. To investigate the effect of pH, additional experiments were conducted at pH values of 4.0, 7.0, and 10.0, adjusted using 0.1 M HCl or NaOH. The pH was selected based on the typical range of petrochemical wastewater and its influence on the adsorbent surface charge and pollutant ionization. After treatment, the mixtures were filtered through Whatman No. 1 filter paper to separate the adsorbent, and the filtrate was analyzed for COD, nitrate, sulfide, turbidity, TDS, TSS, lead (Pb), and zinc (Zn) as described below.

2.2.3. *Analytical Measurements*

COD Measurement: COD was determined using the closed reflux method followed by spectrophotometric analysis at 600 nm (Hach DR6000), as per the Environmental Protection Act (EPA, 1994). Samples were digested with potassium dichromate and sulfuric acid, and the absorbance was compared against a calibration curve (R^2 = 0.99).

Nitrate Measurement: Nitrate concentration was measured immediately or within 48 hours (stored at 4°C) using the ultraviolet method at λ_max = 220 nm (EPA, 1994). A calibration curve was prepared using standard nitrate solutions (0–100 mg/L, R^2 = 0.98).

Sulfide Measurement: Sulfide concentration was determined by iodometric titration. An estimated volume of iodine solution (0.025 N) was added to the sample, followed by 2 mL of 6N HCl to acidify the mixture. If the iodine color disappeared, additional iodine was added until a persistent color was observed. A few drops of starch solution were added as an indicator, and the solution was titrated with 0.025 N $Na_2S_2O_3$ until the blue color disappeared. The sulfide concentration was calculated using Eq. 1 (EPA, 1994):

$$Sulfide\ \left(\frac{mg}{L}\right) = \frac{\{(A\times B)-(C\times D)\}\times 16000}{V} \qquad (1)$$

where A is the volume of iodine solution (mL), B is the normality of iodine solution, C is the volume of sodium thiosulfate (mL), D is the normality of sodium thiosulfate, and V is the sample volume (mL).

Turbidity Measurement: Turbidity was measured using a Hach 2100Q turbidity meter calibrated with standards (0–1000 NTU). Samples were mixed thoroughly, allowed to settle to remove air bubbles, and poured into a clean turbidity meter tube. The tube's outer surface was dried, and the turbidity reading was recorded in nephelometric turbidity units (NTU) (APHA, 2005).

TDS Measurement: TDS was determined by filtering a 50 mL sample through a 0.45 µm filter. The filtrate was transferred to a pre-weighed porcelain capsule, evaporated in a steam bath at 180°C, and dried to constant weight. The capsule was cooled in a desiccator and weighed. TDS was calculated using Eq. 2 (EPA, 1994):

$$TDS\ \left(\frac{mg}{L}\right) = \frac{\{(A-B)\times 1000\}}{V} \qquad (2)$$

where A is the weight of the dried residue plus capsule (mg), B is the weight of the capsule (mg), and V is the sample volume (mL).

TSS Measurement: TSS was measured by allowing a 250 mL sample to settle for 1 hour. A 100 mL aliquot from the center of the sample was filtered through a pre-weighed 0.45 µm filter. The filter was dried at 105°C, cooled in a desiccator, and weighed. TSS was calculated as the weight of the residue divided by the sample volume (EPA, 1994). Heavy Metal Analysis: Concentrations of lead (Pb) and zinc (Zn) were measured using atomic absorption spectroscopy (AAS, PerkinElmer Analyst 400) at wavelengths of 283.3 nm (Pb) and 213.9 nm (Zn). Calibration curves were prepared using standard solutions (0–5 mg/L, $R^2 > 0.99$).

2.2.4. *Statistical Analysis and Adsorption Kinetics*

The experiments followed a completely randomized factorial design with three factors: adsorbent type (organic, inorganic, composite), adsorbent concentration (2 and 4 g/L), and contact time (20, 40, and 60 minutes). Data were analyzed using SAS software (version 9.4). Mean comparisons were performed using Duncan's multiple range test at a significance level of $p < 0.05$. Analysis of variance (ANOVA) was conducted to assess the significance of main effects and interactions, with results reported as F-statistics and p-values. Adsorption kinetics were investigated to determine the rate of pollutant removal. The pseudo-first-order, pseudo-second-order, Elovich, and Freundlich kinetic models were fitted to the experimental data using nonlinear regression in OriginPro (version 2023). The goodness of fit was evaluated using the coefficient of determination (R^2) and chi-square (χ^2) values. Langmuir and the Freundlich isotherm models were also applied to describe the adsorption equilibrium, with parameters calculated to assess the maximum adsorption capacity and adsorption intensity.

3. Results

The experiments evaluated the efficacy of organic (pomegranate peel-derived activated carbon, OA), inorganic (nano-silica, IA), and composite (CA) adsorbents at concentrations of 2 g/L (OA2, IA2, CA2) and 4 g/L (OA4, IA4, CA4) in reducing chemical oxygen demand (COD), nitrate, sulfide, turbidity, total dissolved solids (TDS), total suspended solids (TSS), lead (Pb), and zinc (Zn) from petrochemical wastewater over contact times of 20, 40, and 60 minutes. All treatments were compared against a control (no adsorbent). The results are summarized below, with statistical significance determined using Duncan's multiple range test ($p < 0.05$).

3.1. Pollutant Removal Efficiency

The percentage reductions in COD, nitrate, sulfide, turbidity, TDS, TSS, Pb, and Zn were measured for each treatment and contact time. Initial pollutant concentrations in the wastewater were as follows: COD (1000 ± 50 mg/L), nitrate (65 ± 5 mg/L), sulfide (30 ± 3 mg/L), turbidity (120 ± 10 NTU), TDS (1250 ± 50 mg/L), TSS (250 ± 20 mg/L), Pb (0.75 ± 0.05 mg/L), and Zn (1.2 ± 0.1 mg/L). Table 1 presents the percentage reductions for all pollutants at 60 minutes for the CA4 treatment, which showed the highest efficacy.

Table 1. Percentage Reduction of Pollutants Using Composite Adsorbent (CA4) at 60 Minutes

Pollutant	Initial Concentration	Final Concentration	Percentage Reduction (%)
COD	1000 ± 50 mg/L	380 ± 20 mg/L	62.0 ± 2.0
Nitrate	65 ± 5 mg/L	43 ± 3 mg/L	33.8 ± 1.5
Sulfide	30 ± 3 mg/L	14 ± 1 mg/L	52.7 ± 1.8
Turbidity	120 ± 10 NTU	80 ± 5 NTU	33.3 ± 2.0
TDS	1250 ± 50 mg/L	800 ± 30 mg/L	36.1 ± 1.5
TSS	250 ± 20 mg/L	187 ± 15 mg/L	25.3 ± 1.2
Pb	0.75 ± 0.05 mg/L	0.41 ± 0.03 mg/L	46.0 ± 2.0
Zn	1.2 ± 0.1 mg/L	0.72 ± 0.05 mg/L	39.8 ± 1.8

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The interaction effects of adsorbent treatments and contact time on multiple wastewater parameters are summarized in Figure 1. For COD levels, the CA4 treatment at 60 minutes yielded the lowest average COD, which was significantly different from other treatment combinations. The control treatment consistently showed the highest COD levels across all time points. Extending the contact time to 60 minutes significantly reduced the average COD compared to 20 and 40 minutes for all adsorbent treatments. The results for other treatment combinations (OA2, OA4, IA2, IA4, CA2) showed intermediate COD reductions, with CA2 outperforming OA and IA treatments at all time points.

A similar trend was observed for nitrate levels. The CA4 treatment at 60 minutes resulted in the lowest average nitrate concentration, differing significantly from other combinations. The control had the highest average nitrate at 20 and 40 minutes. The 60-minute contact time significantly reduced average nitrate levels compared to shorter times for all adsorbent treatments. Average nitrate levels for OA2, OA4, IA2, IA4, and CA2 treatments were intermediate, with CA2 showing significantly lower levels than OA and IA treatments. The pattern continued for sulfide, turbidity, TDS, and TSS. In each case, the CA4 treatment at 60 minutes produced the lowest mean concentration, which was significantly different from other treatments. The control consistently yielded the highest values. For all adsorbent treatments, the 60-minute contact time led to a significant reduction in the average concentration of each parameter compared to 20 and 40 minutes.

The performance of the OA2, OA4, IA2, IA4, and CA2 treatments was intermediate, with CA2 consistently demonstrating greater removal efficiency than the corresponding OA and IA treatments across all parameters and time points.

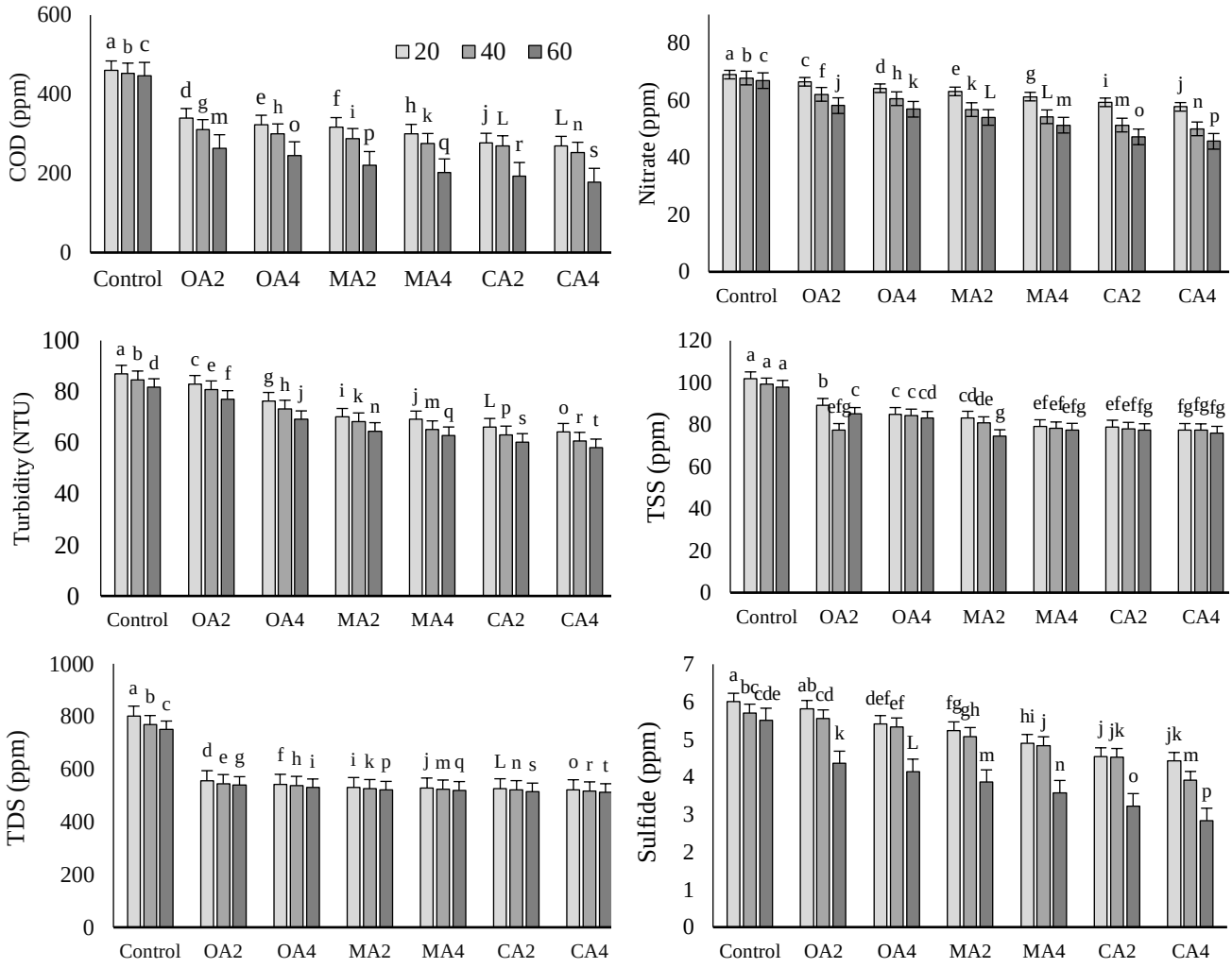

Figure 1. Interaction Effects of Adsorbent Treatments and Contact Time on COD, Nitrate, Turbidity, TSS, TDS, Sulfide and Levels. COD levels (mg/L) for organic (OA), inorganic (IA), and composite (CA) adsorbents at 2 and 4 g/L concentrations over 20, 40, and 60 minutes, compared to the control. Means with different letters indicate significant differences ($p < 0.05$, Duncan's test)

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Figure 2 shows the comparison of the average interaction effect of the two factors of absorbent treatments and time on Pb levels. As can be seen, CA4 absorbent treatment has the lowest average Pb in 60 min and has a significant difference from other treatment combinations. The control treatment has the highest average of this variable in all three times, between 20, 40, and 60 min, and has shown a significant difference with other treatment combinations. Also, for all absorbent treatments, the time of 60 min compared to the times of 20 and 40 min was able to significantly reduce the average Pb. The average Pb levels for other treatments followed a similar trend, with CA2 showing greater reductions than OA and IA treatments.

Figure 3 shows the comparison of the average interaction effect of adsorbent treatments and time on Zn levels. The CA4 treatment had the lowest average Zn concentration at 60 minutes, significantly different from other treatment combinations. The control treatment had the highest average Zn concentration at all time points (20, 40, and 60 minutes), significantly differing from other treatments. For all adsorbent treatments, the 60-minute contact time significantly reduced Zn levels compared to 20 and 40 minutes.

The Zn levels for OA2, OA4, IA2, IA4, and CA2 treatments were intermediate, with CA2 outperforming OA and IA treatments.

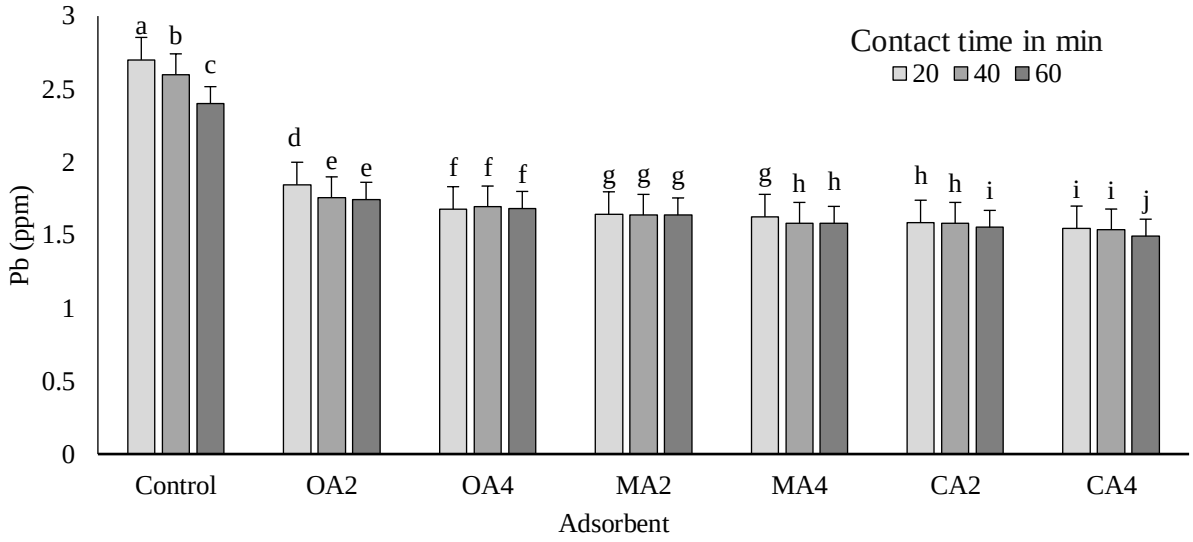

Figure 2. Interaction Effects of Adsorbent Treatments and Contact Time on Pb Levels. Pb concentrations (mg/L) for organic (OA), inorganic (IA), and composite (CA) adsorbents at 2 and 4 g/L concentrations over 20, 40, and 60 minutes, compared to the control. Means with different letters indicate significant differences ($p < 0.05$, Duncan's test)

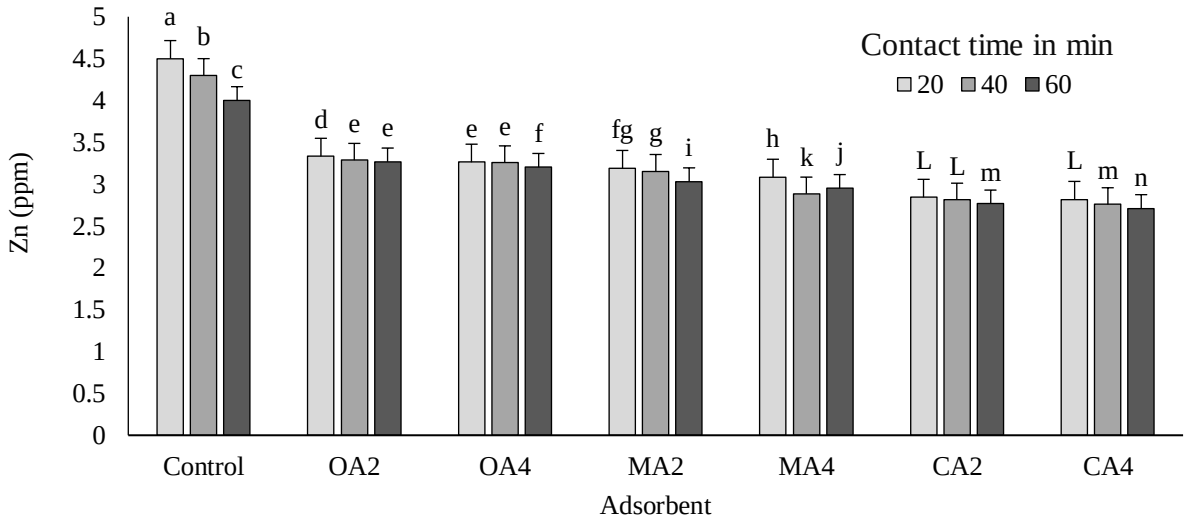

Figure 3. Interaction Effects of Adsorbent Treatments and Contact Time on Zn Levels. Zn concentrations (mg/L) for organic (OA), inorganic (IA), and composite (CA) adsorbents at 2 and 4 g/L concentrations over 20, 40, and 60 minutes, compared to the control. Means with different letters indicate significant differences ($p < 0.05$, Duncan's test)

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3.2. Adsorption Kinetics

The adsorption kinetics of COD onto the CA4 adsorbent was investigated using an adsorbent dose of 4 g/L in 300 mL wastewater with an initial COD concentration of 1000 mg/L, over a contact time of 60 minutes. Figure 4 presents the variation of adsorption capacity (qt) with time, along with the fitted pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order model exhibited the best fit to the experimental data (R^2 = 0.98, χ^2 = 0.02), suggesting that the adsorption process is predominantly physisorption-controlled. The pseudo-second-order model provided a reasonably good but inferior fit (R^2 = 0.95, χ^2 = 0.05). Equilibrium adsorption behavior was evaluated at 60 minutes across initial COD concentrations ranging from 500 to 1500 mg/L. The linearized Freundlich isotherm, shown in Figure 4, demonstrates a good linear fit (R^2 = 0.95, χ^2 = 0.04), indicating multilayer adsorption on a heterogeneous surface of the CA4 adsorbent. The fitted parameters from the pseudo-first-order, pseudo-second-order, Elovich, and Freundlich models are summarized in Table 2.

Table 2. Kinetic Parameters for COD Adsorption by CA4 Adsorbent at 60 Minutes

Model	Parameter	Value	R^2	χ^2
Pseudo-first-order	k_1 (min^{-1})	0.045 ± 0.005	0.98	0.02
	q_e (mg/g)	135 ± 10		
Pseudo-second-order	k_2 (g/(mg·min))	0.0003 ± 0.00005	0.95	0.05
	q_e (mg/g)	142 ± 12		
Elovich	α (mg/(g·min))	25 ± 3	0.9	0.08
	β (g/mg)	0.04 ± 0.01		
Freundlich	K_F (mg/g·(L/mg)^1/n)	15 ± 2	0.92	0.06
	n	2.5 ± 0.3		

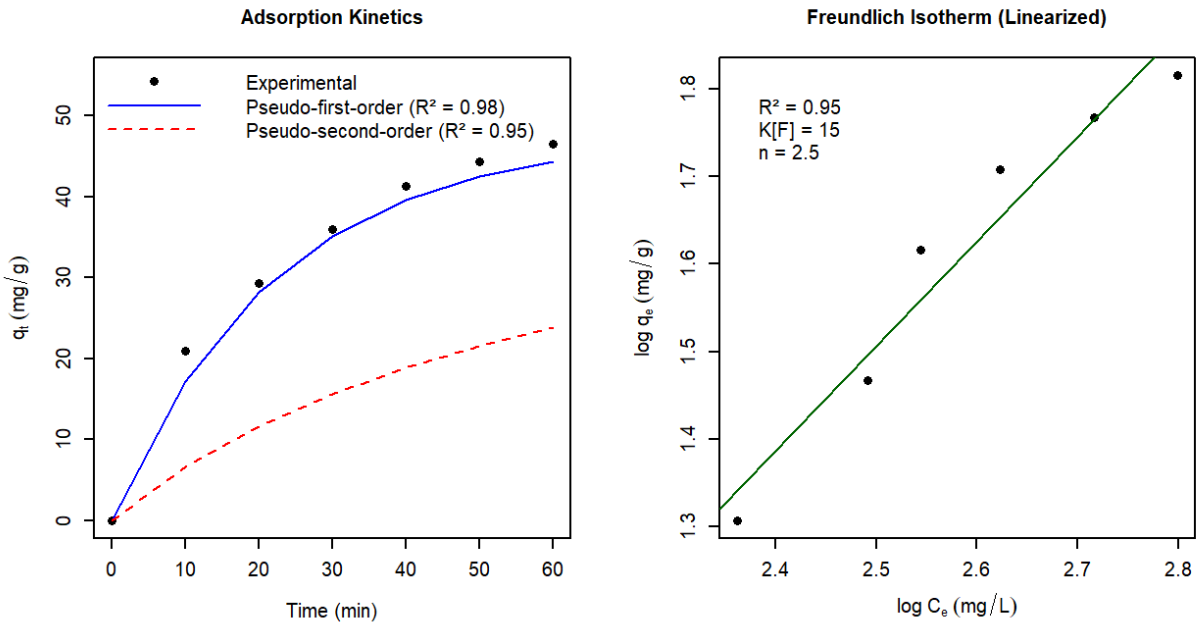

Figure 4. (left) Adsorption kinetics of COD onto CA4 adsorbent showing experimental data (symbols) and fitted curves for the pseudo-first-order (solid line, R^2 = 0.98) and pseudo-second-order (dashed line, R^2 = 0.95) models (initial COD = 1000 mg/L, adsorbent dose = 4 g/L). (right) Linearized Freundlich isotherm plot for COD adsorption at equilibrium (60 min contact time, initial COD range 500–1500 mg/L)

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4. Discussion

4.1. Synergy in composite adsorbents for pollutant removal

The treatment of complex petrochemical wastewater requires materials capable of addressing its mixed pollutant profile. Adsorption's effectiveness in petrochemical wastewater treatment hinges on synergistic interactions between the composite's surface properties and diverse pollutants. At 4 g/L and 60 minutes, the composite adsorbent CA4 reduced COD, nitrate, sulfide, turbidity, TDS, TSS, Pb, and Zn by 25.3–62.0%, outperforming OA and IA adsorbents at 2 and 4 g/L. Complementary pathways explain this superior efficacy. Hydroxyl and carboxyl groups from pomegranate peel enable hydrogen bonding and hydrophobic interactions with organic pollutants like sulfolane. Similar hydrogen bonding and hydrophobic interactions with organic pollutants were also observed by Islam et al. (2025) in polymer–silica composites, illustrating a shared mechanism for organic uptake.

Silica's nanostructured pores capture inorganic ions and heavy metals via electrostatic attraction and surface complexation. Effective capture of heavy metals through electrostatic attraction and surface complexation was also noted by Abdel-Aziz et al. (2019) in silica-based systems, highlighting a common strategy for inorganic species. Lower removal of nitrate and TSS suggests competitive adsorption, where COD and sulfide preferentially occupy active sites due to stronger binding affinities. Preferential binding of organic compounds in multi-pollutant systems was also reported by Sarkar et al. (2025), reflecting the composite's competitive adsorption behavior. Similar competitive dominance by organic compounds was also observed by Gupta et al. (2024) in multi-pollutant systems, which aligns with the observed site occupancy patterns here.

In practical terms, the composite's COD and sulfide reductions exceed typical refinery wastewater treatment efficiencies, as benchmarked by El-Naas et al. (2010), highlighting its superior performance. The ability to simultaneously address organic, inorganic, and particulate contaminants underscores the composite's versatility. Versatile pollutant removal by hybrid adsorbents was also reported by Liu et al. (2021), matching the composite's multi-pollutant efficacy. Similar synergistic performance in mixed adsorbents was also noted by Khader et al. (2021), reinforcing the composite's effectiveness. These synergistic interactions between organic and inorganic components confirm that combined surface properties enhance pollutant removal efficiency. Mechanistic parallels with hybrid and mixed adsorbent systems highlight the practical significance of bio–inorganic composites, advancing strategies for comprehensive wastewater treatment.

4.2. Optimized dosage and time for pollutant removal

Adsorption efficiency in petrochemical wastewater treatment hinges on optimizing dosage and contact time to maximize site availability and pollutant diffusion. The present study demonstrates this principle in a real petrochemical effluent containing multiple contaminants. According to the results, the composite adsorbent CA4 at 4 g/L and 60 minutes reduced COD, nitrate, sulfide, turbidity, TDS, TSS, Pb, and Zn by up to 62.0%, outperforming CA2, OA, and IA adsorbents at 2 and 4 g/L. The higher dosage of 4 g/L increased accessible adsorption sites and surface area, enabling the composite to capture a broad range of pollutants effectively. This enhanced site availability mirrors the performance of pomegranate peel-based adsorbents, as Al-Badaii et al. (2024) found for boron removal at elevated dosages.

The superior performance of the composite arises from its synergistic multicomponent structure. The composite's structure, combining pomegranate peel's organic matrix with silica's nanoscale pores, provided a high surface area that stabilizes pollutant binding across diverse chemical species. Moreover, a 60-minute contact time facilitated diffusion of bulky organics and divalent ions like Pb^{2+} and Zn^{2+} into internal pore structures, ensuring maximum removal efficiency. Extended contact time enhances diffusion in modified peel adsorbents, a mechanism Wang et al. (2022) reported, supporting the composite's time-dependent performance.

The balance of dosage and contact time allowed the composite to approach adsorption equilibrium, particularly for complex pollutants like COD and heavy metals. This optimization strategy aligns with findings by Sharma and Singh (2020), who demonstrated rapid pollutant removal with increased dosage in low-cost adsorbents. These results confirm that the combination of higher dosage (4 g/L) and sufficient contact time (60 min) is critical for maximizing heterogeneous adsorption on composite surfaces. The composite's ability to efficiently remove multiple pollutants at 4 g/L and 60 minutes underscores the critical role of tailored operational conditions in achieving robust treatment outcomes, confirming that optimizing dosage and contact time maximizes site accessibility and diffusion, ensuring effective multi-pollutant removal. The achieved multi-pollutant removal (e.g., 62% COD, ~46-40% metals) via adsorption presents a complementary approach to advanced catalytic degradation, which can achieve near-complete removal of specific recalcitrant organics but may be less effective for mixed inorganic-organic matrices like

petrochemical wastewater (Fekri et al., 2021). This highlights the importance of selecting a treatment process (adsorption vs. advanced oxidation) based on the specific pollutant profile and treatment goals.

4.3. Physical adsorption mechanisms for COD removal

The kinetics of COD removal in petrochemical wastewater treatment depend on rapid physical interactions with the composite's surface. At 4 g/L and 60 minutes, the composite adsorbent (CA4) reduced COD by up to 62.0% across initial concentrations (800–1200 mg/L), as shown in Tables 2 and 3. Consequently, a pseudo-first-order kinetic model best fit the data ($R^2 = 0.98$, $\chi^2 = 0.02$), outperforming pseudo-second-order and Elovich models. This indicates a diffusion-controlled, physical process, contrasting with chemisorption which often follows pseudo-second-order kinetics. Similarly, a Freundlich isotherm ($R^2 = 0.95$) surpassed the Langmuir model. These results demonstrate that van der Waals forces and hydrophobic interactions drive rapid COD uptake. The Freundlich fit specifically suggests multilayer adsorption on a heterogeneous surface, enabling efficient pollutant capture. Niknejad et al. (2021) found that biocomposites with high surface area promote weak, reversible binding for organic pollutants, a finding that corroborates the physical mechanism identified here.
The composite integrates pomegranate peel's organic matrix with silica's nanoscale pores. This structure creates a high surface area. Furthermore, it supports multilayer adsorption of complex COD components. The Freundlich isotherm's fit indicates diverse binding sites on the composite's surface. These sites accommodate varied organic compounds without strong chemical bonds. As a result, COD removal efficiency increases significantly. Al-Badaii et al. (2024) demonstrated similar site heterogeneity in boron adsorption on pomegranate peel, supporting the composite's ability to handle diverse pollutants. Within 60 minutes, the rapid COD reduction highlights the efficiency of surface-driven kinetics. This rapid uptake is particularly effective for complex organic mixtures in petrochemical wastewater. Moreover, Wang et al. (2022) reported fast heavy metal uptake on modified peels, reaching equilibrium in minutes, a kinetic profile consistent with the composite's performance.

The combination of pseudo-first-order kinetics and multilayer adsorption enables the composite to manage high COD loads effectively. From a practical standpoint, this physical mechanism is advantageous as it may allow for easier adsorbent regeneration compared to chemisorption-based systems. These findings confirm that physical adsorption governs COD removal, ensuring efficient pollutant capture. The consistency with biocomposite and silica-based systems underscores the practical significance of surface-driven kinetics, advancing scalable strategies for petrochemical wastewater treatment. Collectively, the synergistic interactions, optimized operational conditions, and physical adsorption mechanisms of the composite highlight its versatility and efficacy in addressing petrochemical wastewater challenges.

4.4. Limitations and Future Research Directions

While this study demonstrates the potential of the pomegranate peel-silica composite, certain limitations must be acknowledged to guide future work. The research was conducted using wastewater from a single petrochemical source; therefore, its performance may vary when applied to effluents with different compositions. Additionally, all experiments were performed at the laboratory batch scale under controlled conditions, such as constant room temperature and mechanical stirring, which do not fully replicate the dynamic nature of industrial treatment systems. Therefore, future research should focus on several key areas to advance this technology. First, evaluating the adsorbent's efficiency with wastewater from different petrochemical processes would be essential to assess its robustness and general applicability. Second, conducting continuous-flow column studies is necessary to simulate real-world treatment conditions and determine critical engineering parameters such as breakthrough curves and dynamic adsorption capacity. Third, a thorough investigation into the economic feasibility and lifecycle assessment of the composite is needed, including dedicated studies on its regeneration potential and reusability over multiple operational cycles to determine long-term sustainability. Finally, exploring the effects of a wider range of operational parameters, such as systematic variations in temperature and influent pH regimes, would provide deeper insight into its performance stability and optimization for long-term application. To advance toward practical implementation, subsequent research must urgently address two key areas, including the regenerability and reusability of the spent composite over multiple cycles, and a comprehensive techno-economic analysis to evaluate operational costs and scalability.

5. Conclusion

This study contributes to the field of sustainable wastewater treatment by demonstrating the effectiveness of a green-engineered composite adsorbent for the complex challenge of petrochemical effluent remediation. By integrating agricultural waste (pomegranate peel) with

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nanostructured silica, we have developed a material that leverages synergistic interactions for the simultaneous removal of a broad spectrum of organic and inorganic pollutants—a significant advancement over single-component adsorbents typically studied in isolation. The research provides crucial mechanistic insights, establishing that the process is governed by physical, multilayer adsorption on a heterogeneous surface, as described by pseudo-first-order kinetics and the Freundlich isotherm. These findings not only clarify the adsorption pathway but also highlight the composite's practical advantage of potentially easier regeneration compared to chemisorption-based systems. Furthermore, the systematic optimization of dosage and contact time provides a foundational template for scaling this technology from batch experiments to continuous treatment processes. The critical path for industrial adoption now requires conclusive demonstration of the adsorbent's regenerability and a rigorous assessment of its economic feasibility. Ultimately, this work positions bio-inorganic composites as a scalable, cost-effective, and environmentally benign strategy, offering a tangible solution to reduce the environmental footprint of the petrochemical industry and contributing to the circular economy by valorizing agricultural by-products.

Authors Contribution
All authors have contributed equally to prepare the paper.

Availability of data and materials
The data that support the findings of this study are available from the corresponding author, upon reasonable request.

Conflict of interests
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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