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Nonylphenol Removal from Water and Wastewater with Alginate-Activated Carbon Beads

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Abstract: In this study, eco-friendly and sustainable alginate-activated carbon (Alg-C)-based beads were synthesized and characterized for the adsorption of nonylphenols (NPs) from aqueous environments under various conditions. The surface characterization, functional groups, and adsorption behavior were analyzed using multiple analytical techniques. The effect of key parameters, including dosage, pH, temperature, and reusability, were evaluated. Isotherm and kinetic studies revealed that the adsorption process followed a pseudo-second-order kinetic model and aligned with the Freundlich isotherm, indicating a heterogeneous surface. The beads exhibited a high removal efficiency of 97% over five reuse cycles in a 50 mL solution of 10 mg L⁻¹ NPs under static conditions, demonstrating their recyclability. Thermodynamic analysis suggested potential electrostatic interactions, supported by positive Gibbs free energy values. The highest removal performance was achieved within 90 min, with adsorption capacities from 0.10 to 0.39 mg g⁻¹. Additionally, the performance of Alg-C beads remained stable across different pH levels, highlighting their robustness. When tested with wastewater samples, Alg-C beads maintained high removal efficiency, with no significant matrix effects observed. These results underscore Alg-C beads as a promising and sustainable solution for the elimination of NPs from contaminated water sources.

Keywords: alkylphenols; adsorption; solventless extraction; Alg-C beads; wastewater treatment; SBSE-TDU-GC-MS; eco-friendly agents



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1. Introduction

Since the early 2000s, the recurrent, abundant, and persistent presence of contaminants of emerging concern (CECs) has become a significant threat to water quality worldwide [1]. CECs, which include unregulated chemicals, either naturally occurring or man-made, are suspected to have adverse biological effects on living organisms [2]. Among the contaminants, persistent organic pollutants (POPs) and endocrine disrupting chemicals (EDCs) have raised particular concern due to their high toxicity and environmental persistence [3]. A prominent example of such pollutants is nonylphenols (NPs), which have been widely used in industrial and consumer products since their development in the 1940s. NPs are primarily used as intermediates in the production of nonylphenol ethoxylates (NPEs), which are prevalent in industries like textiles, plastics, dyes, emulsifiers, and detergents [4]. Due to their extensive usage, NPs and NPEs are common in domestic and industrial effluents, leading to their persistence in wastewater treatment plants (WWTPs) [5]. However,

WWTPs are not specifically designed to remove these pollutants, resulting in NPs and NPEs entering natural water ecosystems [6]. This widespread contamination is present globally in aquatic environments at $\mu\text{g L}^{-1}$ levels [7].

The presence of NPs in water poses significant environmental and public health risks. Due to their high lipophilicity, NPs are easily adsorbed by aquatic organisms and can mimic hormones, leading to bioaccumulation and endocrine disruption [8]. These compounds have been shown to cause development and reproductive abnormalities in aquatic life [9], as well as influencing the behavior and growth of marine organisms, including invertebrates and fish [10]. Furthermore, NPs have been found in various seafood species, such as prawns, mussels, crabs, and fish, which poses a direct route of human exposure to these harmful chemicals [9,11,12]. The detection of NPs in human samples, such as blood ($0.018 \mu\text{g L}^{-1}$) [13], urine ($>1 \mu\text{g kg}^{-1}$) [14], and breast milk ($>47 \mu\text{g L}^{-1}$) [15], has raised additional concerns regarding their potential to disrupt hormonal systems. Given these risks, countries like Canada, Japan, and the European Union have banned the use of NPs and the United States has listed them as a priority pollutant, setting recommended limits for their presence in freshwater ($6.6 \mu\text{g L}^{-1}$) and salt water ($1.7 \mu\text{g L}^{-1}$) [16,17].

In response to the widespread spread of NPs in aquatic environments, various technologies have been developed for their removal from water. Biological treatments, such as the use of microorganisms in activated sludge systems, have demonstrated some success in degrading organic pollutants, including NPs, through anaerobic and aerobic processes [18]. For example, an anaerobic treatment process has been reported to achieve up to 67% removal of NPs [19]. Additionally, advanced oxidation processes (AOPs), including photocatalysis, have shown high efficacy in degrading NPs from water using TiO_2 nanotubes, achieving nearly 100% removal for a 5 mg L^{-1} NP solution in 40 min. However, AOPs have limitations, such as the lack of selectivity of catalysts and the short lifespan of their free radicals generated during treatment [20,21].

In recent years, adsorption methods have gained popularity due to their simplicity, cost effectiveness, and rapid applicability in removing contaminants from wastewater [22]. Activated carbon, in particular, has been extensively studied for its high adsorption capacity, attributed to its high surface area, internal porosity, and chemical oxygenated groups [23]. Also, activated carbon properties are ecofriendly and sustainable, and activated carbon has found applications as an adsorbent in WWTPs [24]. Despite these advantages, activated carbon has limitations, including low mechanical resistance, low hydraulic conductivity, and a lack of reusability, which hinder its widespread application. To address these challenges, researchers have focused on improving the performance of activated carbon by incorporating materials like sodium alginate and calcium ions to form composite materials, known as Alg-C beads [23,25,26].

While several studies have explored the use of Alg-C beads for removing other contaminants such as bisphenol A [27], ibuprofen [28] and methylene blue [29], there is limited research specifically targeting the removal of NPs using Alg-C composites. This presents a significant research gap, especially considering the growing concern about NPs in aquatic ecosystems and their potential impacts on human and environmental health. Furthermore, the reusability and performance of Alg-C beads under dynamic environmental conditions have not been extensively evaluated in real wastewater matrices.

The primary objective of this study is to evaluate the effectiveness of Alg-C beads in eliminating NPs from water and wastewater samples. Specifically, this study aims to (1) investigate the adsorption capacity of Alg-C beads for NPs in varying environmental conditions (dosage, pH, and temperature), (2) assess the reusability of Alg-C beads to evaluate their potential for sustained pollutant removal in wastewater treatment, and (3) provide practical insights into the real-world applicability of Alg-C beads by using

actual wastewater samples. This study contributes to the development of eco-friendly, sustainable, and cost-effective strategies for the removal of NPs from wastewater, which is crucial for addressing the ongoing environmental and public concerns associated with these contaminants.

2. Materials and Methods

2.1. Materials

All reagents were obtained from commercial sources and used without further modification. 4-Nonylphenol technical grade, alginate sodium salt, activated carbon, and acetic anhydride (GR ACS grade) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Calcium chloride dihydrate (ACS grade) and methanol (HPLC grade) were obtained from VWR chemicals (Aurora, CO, USA), while sodium carbonate was sourced from ACROS chemicals (ordered via VWR). The internal standard solution of mirex (99.0%, Dr. Ehrestorfer GmbH, Augsburg, Germany) was prepared in acetonitrile at a 1 mg/L concentration. Solution pH adjustments were carried out using sodium hydroxide from ACROS chemicals and hydrochloric acid (ACS grade) from Ward's Science. Deionized water (DI) was obtained from a Millipore-Q Advantage-10 system (Bedford, MA, USA).

2.2. Preparation of Alg-C Beads

In 50 mL of deionized water, 0.5 g of powdered activated carbon and 0.5 g of sodium alginate (in a 1:1 mass ratio) were added, and the mixture was then stirred at 700 rpm for 30 min. Subsequently, the Alg-C bead solution was transferred into a 10 mL syringe and added dropwise into a 200 mL solution of 0.2 M calcium chloride. This mixture was stirred at 700 rpm for three hours, forming Alg-C bead hydrogels. These Alg-C bead hydrogels were filtered, rinsed with deionized water to remove any residual calcium chloride from the surface, and placed on a glass plate to air dry overnight at room temperature to form Alg-C beads. For the control group, only sodium alginate (0.5 g) was used, and the same procedure was followed to form the alginate beads without activated carbon.

2.3. Characterization of Alg-C Beads

The surface morphology of the Alg-C beads was analyzed using a Hitachi S-4800 scanning electron microscope (SEM) (Tokyo, Japan). The SEM was operated at an accelerating voltage of 10 kV to obtain high-resolution images of the bead surface. A Brunauer–Emmett–Teller (BET) surface analysis was performed using a Micromeritics ASAP-2020 sorptometer (Norcross, GA, USA) to evaluate potential surface changes before and after adsorption. The surface area, total pore volume, and pore size of the Alg-C beads were measured using nitrogen gas isotherms at a temperature of 77 K (−192 °C). Furthermore, Fourier transform infrared (FTIR) spectroscopy was performed using an Agilent Cary FTIR spectrometer (Wilmington, DE, USA) and employed to identify alterations in functional groups within the spectral range of 4000–500 cm^{−1} before and after adsorption.

2.4. Dosage Experiments

Each dosage of Alg-C beads (1, 2, 3, 4, and 5 g) was independently assessed in 50 mL of a solution containing 10 mg L^{−1} of the NP solution to determine the removal efficiency under static conditions. Samples of 200 µL of the NP solution were withdrawn at 0, 5, and 10 min and subsequently at 10 min intervals for a total duration of 90 min. The removal percentage (R%) and adsorption capacity (q_e) of NPs were determined using Equation (1) and Equation (2), respectively [30].

$$R \% = \frac{C_o - C_t}{C_o} \times 100\% \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (2)$$

where the components of the equation are as follows:

C_0 = the initial concentration of NPs (mg L^{-1});

C_t = the concentration of NPs at a specific time during the sampling, starting from 0 min (mg L^{-1});

C_e = the concentration (mg L^{-1}) of NPs at equilibrium;

V = the volume of the NP solution (L);

M = the mass of the Alg-C bead dosage (g).

These aliquots were then transferred to 20 mL amber vials containing 19.4 mL of the 1% (w/v) sodium carbonate solution and 200 μL of the 1 mg L^{-1} mirex solution (as the internal standard). Following this, 200 μL acetic anhydride was added to derivatize the NPs in the solution. Adsorption extraction samples were conducted in triplicates and subjected to NP analysis using stir bar sorptive extraction in-line coupled with thermal desorption and gas chromatography-mass spectrometry (SBSE-TDU-GC-MS).

Moreover, a comparative analysis was performed using 5 g of alginate beads to determine the adsorption removal capabilities of Alg-C beads and alginate alone. This alginate dose was selected as the highest dosage to evaluate the performance and compare it to the maximum removal capacity of Alg-C beads at the same dose. The same procedure was conducted to assess the adsorption performance of alginate beads over a 90 min duration in a 10 mg L^{-1} NPs solution.

2.5. Kinetics, Isotherms, and Thermodynamics Determination

The NP adsorption by the Alg-C beads was evaluated using the dosage experiments based on their kinetics and isotherms in 10 mg L^{-1} of the NP solution. The kinetic models were implemented under different doses (i.e., 1, 2, 3, 4, and 5 g) of Alg-C beads in response to the adsorption of NPs. Utilizing Equations (3) and (4), the pseudo-first- and pseudo-second-order kinetics were evaluated, respectively [31]. The parameters included q_e ($\text{mg} \cdot \text{g}^{-1}$), the adsorption capacity of each dosage at equilibrium from various doses of Alg-C beads; q_t ($\text{mg} \cdot \text{g}^{-1}$), the amount of each dose at a specific time (t), k_1 (min^{-1}); and k_2 ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$), representing the rate constants for the pseudo-first- and pseudo-second-order kinetic models, respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

The adsorption models investigated included the two-parameter Langmuir and Freundlich models. These models offered valuable insights into the adsorption behavior of NPs and the interaction between NPs and Alg-C beads. The Langmuir model is represented in Equation (5), where C_e denotes the concentration of NPs (mg/L) at equilibrium, K_L is the Langmuir constant (L mg^{-1}), q_e (mg g^{-1}), and $q_{\max}$ (mg g^{-1}) represents the maximum adsorption capacity [32]. Conversely, the Freundlich model, expressed in Equation (6), features K_F , representing the adsorption capacity (mg g^{-1}), and $1/n$, representing the adsorption intensity [33,34].

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{q_{\max} K_L} \quad (5)$$

$$\ln(q_e) = \frac{1}{n} \ln C_e + \ln K_F \quad (6)$$

The NP adsorption thermodynamics was evaluated using Gibbs free energy (ΔG , J/mol), enthalpy (ΔH , J/mol), and entropy (ΔS , $\frac{\text{J}}{\text{mol}} \cdot \text{K}$) with the Equations (7) and (8) [29]. The parameters are as follows: Q_e/C_e denotes the equilibrium constant (mL/g), R represents the gas constant (8.3145 J/mol·K), T is the adsorption temperature (K), and ΔS° (J/mol·K) and ΔH° (J/mol) illustrate the change of entropy and enthalpy, respectively.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

$$\ln\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

2.6. pH Experiments

To determine the effect of pH on the potential ability of Alg-C beads to remove NPs, three pH conditions were selected: acidic (pH 3), neutral (no pH adjustment), and alkaline (pH 10). A dosage of 5 g of Alg-C beads was used in a 50 mL solution containing 10 mg L⁻¹ NPs. Samples of 200 μL were collected as described in the adsorption experiments at three time intervals: 0 min, 30 min, and 60 min. All treatments were conducted in triplicate. pH adjustments were made using 2 M HCl acid for acidic conditions and 2 M NaOH for alkaline conditions. Extracted aliquots were transferred into a 20 mL vial containing 19.4 mL 1% (*w/v*) sodium carbonate and 200 μL of 1 mg L⁻¹ mirex. Acetic anhydride (200 μL) was added to derivatize the solution. NPs were analyzed by SBSE-TD-GC-MS analysis [35].

2.7. Reusability of Alg-C Beads Experiments

We investigated the reusability of Alg-C beads in the removal of NPs. The experimental configuration involved utilizing 5 g of Alg-C beads in a 50 mL solution containing 10 mg L⁻¹ NPs. The Alg-C beads were immersed in the solution and allowed to interact with the NPs for a period of 1 h. To track the removal process and achieve equilibrium, 1 mL samples were drawn from a 50 mL solution containing 10 mg L⁻¹ NPs at intervals of 0, 5, and 10 min and subsequently at 10 min intervals until equilibrium was reached. From each extracted sample, 200 μL was reserved for SBSE-TD-GC-MS analysis. After NP adsorption, the Alg-C beads were filtered and rinsed thoroughly with deionized water to eliminate any possible NP remnant. The beads were air-dried overnight and then preserved for the next cycle. The experiment was repeated until a notable decrease in the removal efficiency of the Alg-C beads was observed.

2.8. Wastewater Experiments

Alg-C beads' efficacy in real-world situations was evaluated using wastewater samples provided by El Paso Water in El Paso, TX, USA. A 50 mL aliquot of wastewater was transferred to an amber vial, followed by adding 5 g of Alg-C beads. Extractions were performed at 0 min, 5 min, 10 min, and every 10 min interval for a duration of 90 min. From each sample, a volume of 200 μL was transferred to a 20 mL amber vial containing 19.4 mL 1% (*w/v*) sodium carbonate and 1 mg L⁻¹ mirex. Subsequently, 200 μL acetic anhydride was added as the derivatization agent, and the samples were subjected to SBSE-TDU-GC-MS analysis.

2.9. SBSE-TDU-GC-MS Analysis, Calibration Curve, and Statistical Analysis

The stir bar sorptive extraction procedure involved placing a magnetic stir bar (Twister™, 10 mm, 1 mm, Gerstel, Mülheim and der Ruhr, Germany) coated with polydimethylsiloxane (PDMS) into each sample, which was then stirred for 4 h at 1000 rpm under room temperature. After the stirring period was concluded, the stir bar was carefully

removed from the amber glass using tweezers, rinsed with deionized water, dried with lint-free paper, and transferred into a thermal desorption tube, which was then placed into the thermal desorption unit (TD3.5+ Gerstel) coupled with a gas chromatography-mass spectrometer (GC-MS system 8890/5977B-N, Agilent Technologies, Wilmington, DE, USA) for further qualitative and quantitative analysis of NPs. The GC-MS was equipped with a HP-5 MS UI capillary column (30 m × 0.25 µm, Agilent, USA). The instrument parameters are provided in Supplemental Table S1.

Six calibration standards were prepared within the range of 0–100 µg L^{−1}. The study identified eight distinct NPs (Figure S1), each with an individual calibration curve established from their respective retention times and ions. The calibration curves demonstrated a high level of accuracy, as evidenced by a correlation coefficient (R²) of 0.99 or higher (shown in Table 1). The limit of detection (LOD) for NPs was previously determined at 5.0 µg L^{−1} (unpublished data).

Table 1. Parameters used to determine the qualitative and quantitative analysis of NPs.

	NP1	NP2	NP3	NP4	NP5	NP6	NP7	NP8
RT	19.35	19.46	19.55	19.65	19.81	19.94	19.99	20.10
Ion	121	135	149	135	149	163	135	149
R ²	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99

To evaluate the significant variations ($p < 0.05$) in NP removal percentages across different pH treatments and usage cycles, a Tukey honest significant difference test (Tukey HSD) for multiple comparison analysis was employed. Batch experiments were conducted in triplicate to ensure the reliability and reproducibility of the findings. The statistical analysis was performed using R-studio (version 1.4.1564) and MS Excel.

3. Results and Discussion

3.1. Characterization of Alg-C Beads

The SEM image in Figure 1 illustrates that the surface of the Alg-C beads is smooth, with some visible pores. These pores have been reported to facilitate molecular diffusion and may extend deep into the material, providing free space that helps the adsorption process in aqueous environments [29]. Surface analysis of the Alg-C beads, both before and after the adsorption experiment with NPs, revealed a similar soft texture and non-uniform appearance. Similar images have been reported in the literature [36].

The BET surface analysis of Alg-C beads was conducted before and after they were mixed with NPs, and the results are presented in Figure S2. Key physical parameters including the BET surface area, micropore volume, average pore diameter, and particle size are summarized in Table 2. The initial BET surface area and average pore diameter of Alg-C beads were found to be 662.90 m² g^{−1} and 55.43 Å, respectively. These values are consistent with previously reported data for alginate-activated carbon composites, which have shown surface areas ranging from 281.4 m² g^{−1} [37] and 890 m² g^{−1} [29] and pore diameters around 54.3 Å [37], supporting the high porosity of the synthesized Alg-C beads. Moreover, the surface area of the Alg-C beads was significantly higher than that of calcium alginate materials, 6.25 m² g^{−1} [37], but lower than that of activated carbon, 1621.8 m² g^{−1} [29,38], exhibiting a similar trend reported in related studies.

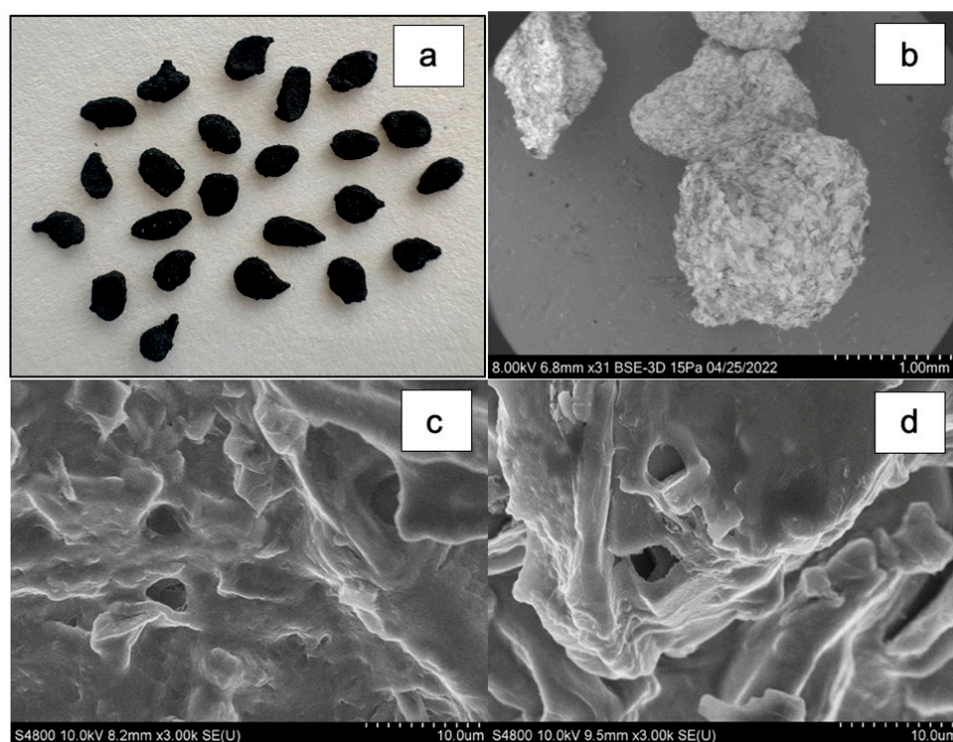


Figure 1. Alg-C bead SEM micrograph before and after being mixed with NPs: (a) an image of Alg-C beads; (b,c) SEM images showing the surface morphology of the Alg-C beads' surface before being mixed with NPs; (d) the Alg-C beads' surface after being mixed with NPs.

Table 2. Surface properties of Alg-C beads before and after being mixed with NPs.

Alg-C Bead Sample	Surface Area (m ² g ^{−1})	Micropore Volume (cm ³ g ^{−1})	Average Pore Diameter (Å)	Average Particle Size (Å)
Before NP sorption	662.90	0.15	55.43	90.51
After NP sorption	341.90	0.080	53.23	175.50

The Alg-C beads revealed notable changes after interacting with NPs, including a reduction in the surface area and micropore volume, as well as an increase in particle size. These variations may be attributed to the adsorption of NPs onto the surface and within the pores, leading to pore blockage and a decrease in available active sites. Such alterations indicate the possible occupancy of spaces post-sorption of NPs. The adsorption behavior and pore size of the Alg-C beads are consistent with reports on the adsorption of heavy metals and organic pollutants [37].

The characterization of the functional groups of Alg-C beads and alginate both mixed with NPs was revealed in the FTIR spectra (Figure 2). Notably, a prominent band at the 3200–3500 cm^{−1} region suggests the presence of phenolic groups due to -OH vibrations [39]. Peaks found at 1550 cm^{−1} indicate the presence of carboxylic acid with the C=O group vibration [40]. C-H vibration is located at approximately 2926 cm^{−1}. Additionally, the region 1600–1650 cm^{−1} indicates the presence of C=O and C=C (from the aromatic ring). The peak at 1230 cm^{−1} is attributed to ester (R-CO-OR) and ether (R-O-R) [39].

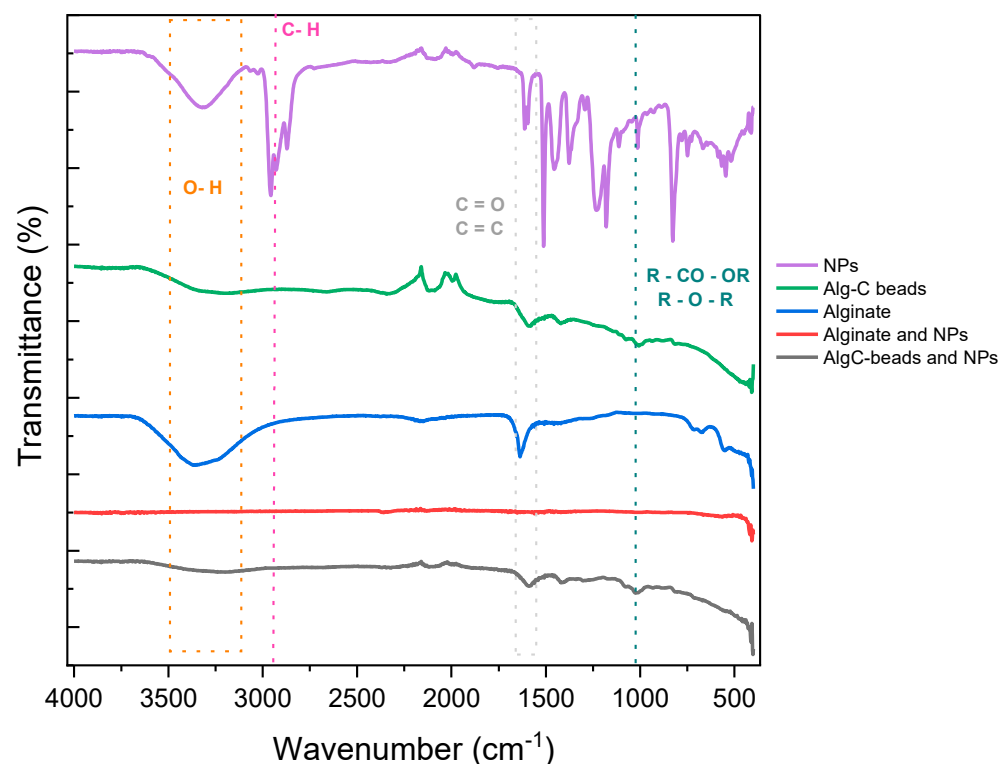


Figure 2. FTIR spectra of Alg-C beads, alginate, Alg-C beads in treatment with NPs, and alginate beads in treatment with NPs.

In this study, surface analysis of the alginate beads was performed using the BET analysis (unpublished data), in which they exhibited significant rigidity, which likely hindered nitrogen gas adsorption. This observation is similar with previous findings [41]. Due to these properties, some of the functional groups were not clearly identified to have participated in the adsorption of NPs. Although direct interactions between alginate and NPs were not apparent, a notable shift in the alginate peak from 1623 cm^{-1} to 1597 cm^{-1} was observed, suggesting a modification in the chemical environment or bonding after the integration into Alg-C beads. This shift is likely indicative of π - π interactions between alginate and the NPs [39].

Additionally, after NP adsorption, the decreased intensity and shifting of the hydroxyl and carboxylic group bands suggest interactions at the active sites of the Alg-C beads. These changes likely result from incorporating contaminants onto the adsorbent surface [42].

3.2. Dosage Experiments

The removal of NPs from water was evaluated in a 50 mL solution of a 10 mg L^{-1} NP aqueous solution. Five doses of Alg-C beads were analyzed at 1, 2, 3, 4, and 5 g. As shown in Figure 3, removing NPs by the Alg-C beads reached equilibrium within 90 min. The removal efficiency increased from 85.91% to 97.64% as the amount of Alg-C beads increased from 1 to 5 g. This behavior is associated with increased active sites in Alg-C beads as the dose increases, leading to higher removal efficiency. This phenomenon is very common and is well-documented in the literature [43]. Among the tested dosages, the 5 g dose demonstrated the highest removal efficiency, achieving 97.64% removal of the target material. This finding supports the selection of the 5 g dose as the most effective option for further experiments, prompting its use in subsequent batch studies to analyze pH, thermodynamics, and wastewater.

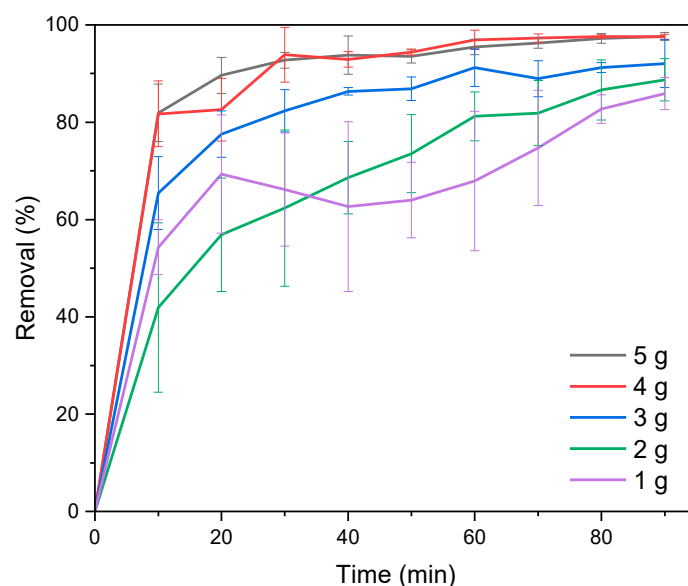


Figure 3. NP removal using 1–5 g of Alg-C bead dosage ($n = 3$). The error bars represent the standard deviation of each dosage level's mean from triplicate experiments.

To determine whether the removal of NPs by the Alg-C beads resulted from alginate or activated carbon, the NP removal efficiency of Alg-C and Alg was investigated. As shown in Figure 4, alginate demonstrated moderate removal of NPs, but the Alg-C beads were significantly more effective. This enhanced removal may likely be due to the activated carbon encapsulated in the alginate, which increased NP removal from 76% with alginate alone to 95%. It has been previously reported that alginate-activated carbon composites are mesoporous materials containing many pores in their inner and outer surface, facilitating the capture of pollutants [44]. Similarly, studies have shown that activated carbon enhances alginate's surface area and pore volume, improving its ability to adsorb pollutants, as observed in this study [45].

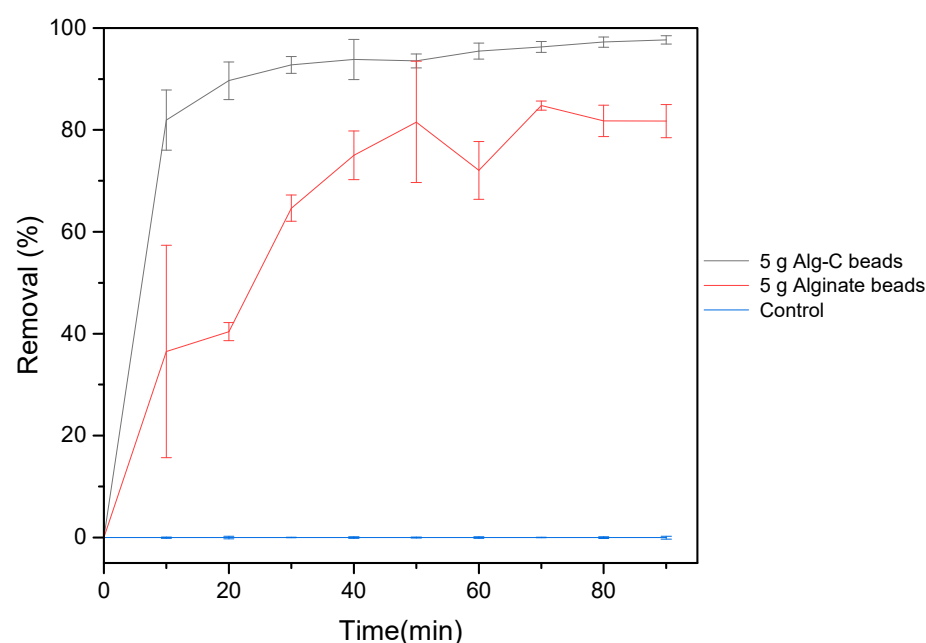


Figure 4. Comparative analysis of NP removal using 5 g of Alg-C beads and 5 g of alginate beads ($n = 3$). The control was obtained directly from NP solution extractions without treatment with Alg-C beads. The error bars represent the standard deviation of the mean ($n = 3$).

3.3. Adsorption Capacity, Kinetics, Adsorption Isotherms, and Thermodynamics

3.3.1. Adsorption Capacity

The adsorption capacity of the Alg-C beads was evaluated using dosages ranging from 1 to 5 g and was calculated using Equation (2). The results, depicted in Table 3, indicate a decrease in adsorption capacity from 0.389 to 0.103 mg g^{−1} as the dosage increases from 1 to 5 g. This observation aligns with previous findings reporting an inversely proportional relationship between adsorption capacity and adsorbent mass. The decrease in adsorption capacity can be attributed to the reduced availability of surface-active sites and pore spaces as the mass of the adsorbent increases [36].

Table 3. Adsorption capacity of each dosage of Alg-C beads evaluated using a 10 mg L^{−1} NP solution in a 50 mL volume solution.

Dose (g)	1	2	3	4	5
q _e (mg g ^{−1})	0.39	0.25	0.22	0.17	0.10

In this study, the Alg-C beads exhibited a lower adsorption capacity compared to previously reported work (287 mg g^{−1}) [36]. Notably, the use of a higher dosage (grams vs. milligrams) achieved equilibrium in a shorter time (90 min. vs. 1000 min). Thus, a better comparison with published results could be followed up by using comparable doses and longer contact durations.

3.3.2. Kinetics

To evaluate the chemical kinetics of the adsorption process, both pseudo-first-order and pseudo-second-order reactions were investigated using Equations (3) and (4). The results were depicted in Figure 5. These findings indicate that the pseudo-second-order kinetic model ($R^2 = 0.95\text{--}0.99$) was more suitable for fitting the Alg-C beads' adsorption than the pseudo-first-order kinetic model ($R^2 = 0.50\text{--}0.97$). Parameters were calculated and are summarized in Table 4. Additionally, a strong correlation was observed between the experimental and theoretical adsorption capacity values when using the pseudo-second order model. The pseudo-second-order model was also consistent with prior reported research on the adsorption of Alg-C beads for pollutant removal [23,36,39].

Table 4. Parameters obtained for pseudo-first- and pseudo-second-order models.

Pseudo-First Order				Pseudo-Second Order			
Dose (g)	q _e (mg·g ^{−1})	k ₁ (min ^{−1})	R ²	Dose (g)	q _e (mg·g ^{−1})	k ₂ (mg·g ^{−1} ·min ^{−1})	R ²
5	0.0001	0.00142	0.0150	5	0.001045	372.2	0.9986
4	0.0002	0.0029	0.0006	4	0.001763	277.7	0.9988
3	0.0002	0.0086	0.0066	3	0.002237	143.2	0.9976
2	0.0001	0.0652	0.3248	2	0.002615	121.7	0.9968
1	0.0007	0.0187	0.0554	1	0.003681	37.38	0.9591

3.3.3. Isotherm Models Study of NPs Adsorption

Langmuir and Freundlich adsorption models were assessed to elucidate the adsorption behaviors and characterize the interaction between NPs and Alg-C beads by using Equations (5) and (6), respectively. As shown in Figure 6 and Table 5, the Freundlich isotherm model demonstrated better correlation ($R^2 = 0.967$) compared to Langmuir model ($R^2 = 0.891$), indicating that Alg-C adsorption of NPs is likely to be a multilayer adsorption

mechanism. The higher correlation coefficient with the Freundlich model suggests that NP adsorption onto Alg-C beads is influenced by site heterogeneity and varied energies. The parameter “n” (Table 5) in the Freundlich isotherm ($n = 1.28$) suggests favorable adsorption and a predominance of a physical adsorption process, consistent with previous findings [36].

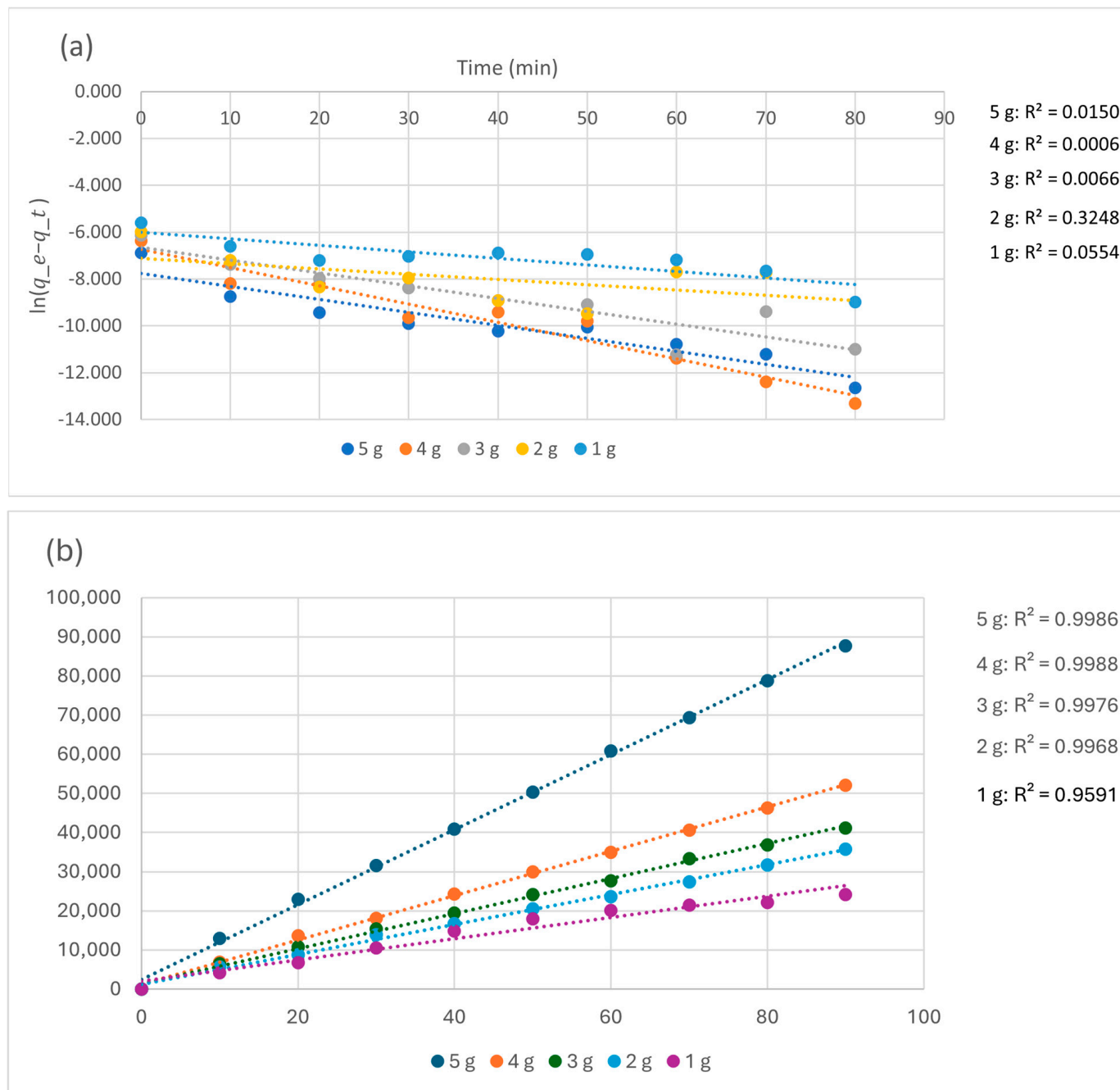


Figure 5. The model fittings indicate the adsorption kinetics: (a) pseudo-first-order model of the adsorption of NPs by Alg-C beads; (b) pseudo-second-order model fitting of the adsorption of NPs by Alg-C beads.

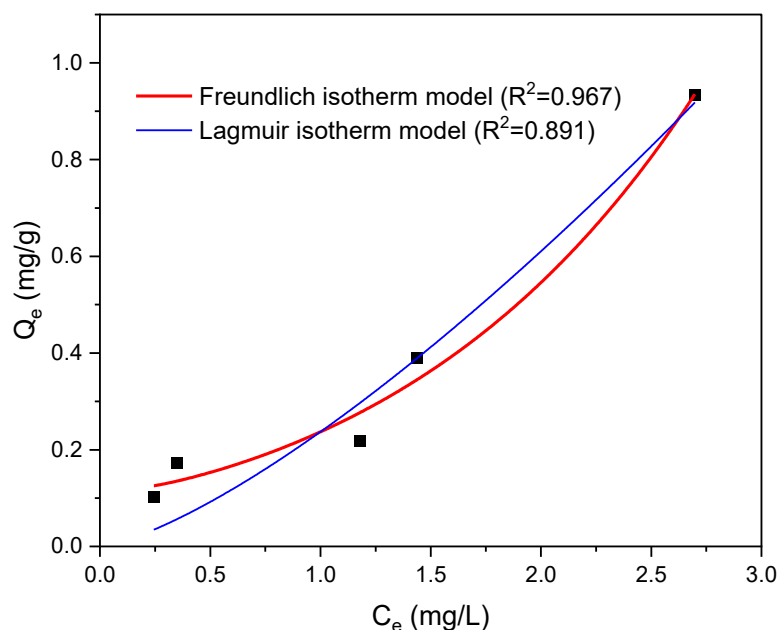


Figure 6. Adsorption of NP model isotherms: Langmuir model and Freundlich model using Alg-C bead dosage of 1–5 g.

Table 5. Adsorption isotherm parameters based on adsorption interaction between NPs and Alg-C beads.

Isotherm	Parameters	Adsorption Values
Langmuir	$q_{\max}$ (mg g ^{−1})	0.35
	K_L (L mg ^{−1})	0.97
	R^2	0.89
Freundlich	n	1.28
	K_F (mg g ^{−1})	0.068
	R^2	0.96

3.3.4. Thermodynamics

To study the effect of temperature on the efficacy of Alg-C beads in removing NPs, 5 g of Alg-C beads was exposed to three temperature settings: 4 °C, 21 °C, and 40 °C. Figure 7 illustrates that Alg-C beads achieved complete NP removal at 40 °C. Furthermore, at 21 °C and 4 °C, 5 g of Alg-C beads exhibited high NP removal capacities of 97% and 96%, respectively.

To evaluate the thermodynamic interactions between Alg-C beads and NPs, Equations (7) and (8) were applied, as presented in Table 6, along with the plot of $\ln(q_e/C_e)$ vs. $1/T$ shown in Figure S3. The parameters calculated and presented in Table 6 indicate that the adsorption is feasible and spontaneous at the given temperatures, as evidenced by the Gibbs free energy ($-\Delta G^\circ$). A positive entropy change suggests increased randomness at the solid–solution interface during the adsorption of NPs onto Alg-C beads in the system ($\Delta S^\circ = 67.07$) [46]. A positive enthalpy change ($\Delta H^\circ = 23.02$) signifies an endothermic process, with its extent increasing with temperature, which is consistent with previous studies on dye adsorption using alginate and activated carbon beads [29]. High temperature is favorable for NP adsorption. Notably, the Alg-C beads achieved a 95% removal rate within 5 min of the experiment at 40 °C.

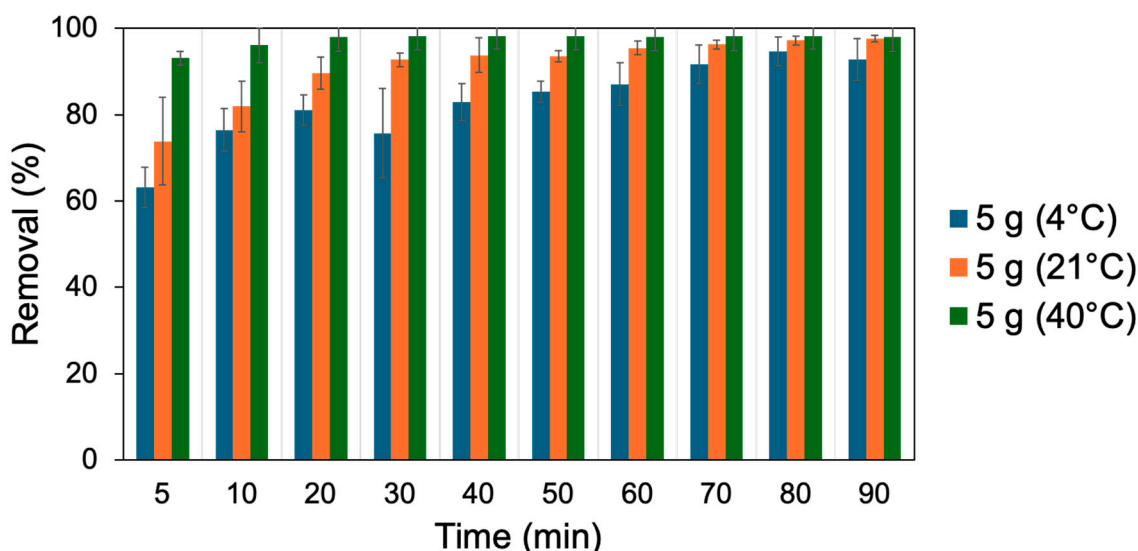


Figure 7. Effect of temperature in the removal of NPs using Alg-C beads. The error bars represent the standard deviation of each temperature level's mean calculated from triplicate experiments.

Table 6. Thermodynamic parameters for NP adsorption using 5 g of Alg-C beads at three different temperatures: 4 °C, 21 °C, and 40 °C.

Temperature (K)	ΔG° (KJ mol ^{−1})	ΔH° (KJ mol ^{−1})	ΔS° (KJ mol ^{−1})
277.15	−18.60	23.020	67.070
294.15	−19.73		
313.15	−21.010		

3.4. pH

The pH solution plays a pivotal role in the adsorption capacity, as it directly affects the surface properties of adsorbents. Variations in pH can indicate alterations in the chemical functional groups on the surface, consequently impacting the removal rate of contaminants. To assess the impact of pH on the efficacy of Alg-C beads in removing NPs, pH conditions were examined from pH 3 to 10. Figure 8 depicts the removal of NPs by Alg-C beads at 30 and 60 min. Based on the Tukey HSD analysis, there are no significant differences ($p < 0.05$) in the removal percentages among the various pH conditions at both the 30 and 60 min extraction times. These findings suggest that the removal efficiency of NPs using Alg-C beads remains unaffected by pH variations, and that the application of Alg-C beads in different environments could be more flexible.

3.5. Reusability

The Alg-C beads underwent seven cycles for reusability over seven cycles. Each cycle involved immersing and reusing 5 g of Alg-C beads in a 50 mL solution containing 10 mg L^{−1} NPs for 1 h. The reusability efficiency remained close to 97% up to the fifth cycle, as shown in Figure 9. A Tukey HSD test, conducted at a 95% confidence level, revealed no significant difference in removal capacity among the first five cycles. However, a notable decrease was observed in cycles 6 and 7 compared to cycles 1 to 5. Similarly, the reusability of an alginate-activated carbon composite has been reported for removing pharmaceutical contaminants and dyes, maintaining high removal rates for up to five cycles [47–49].

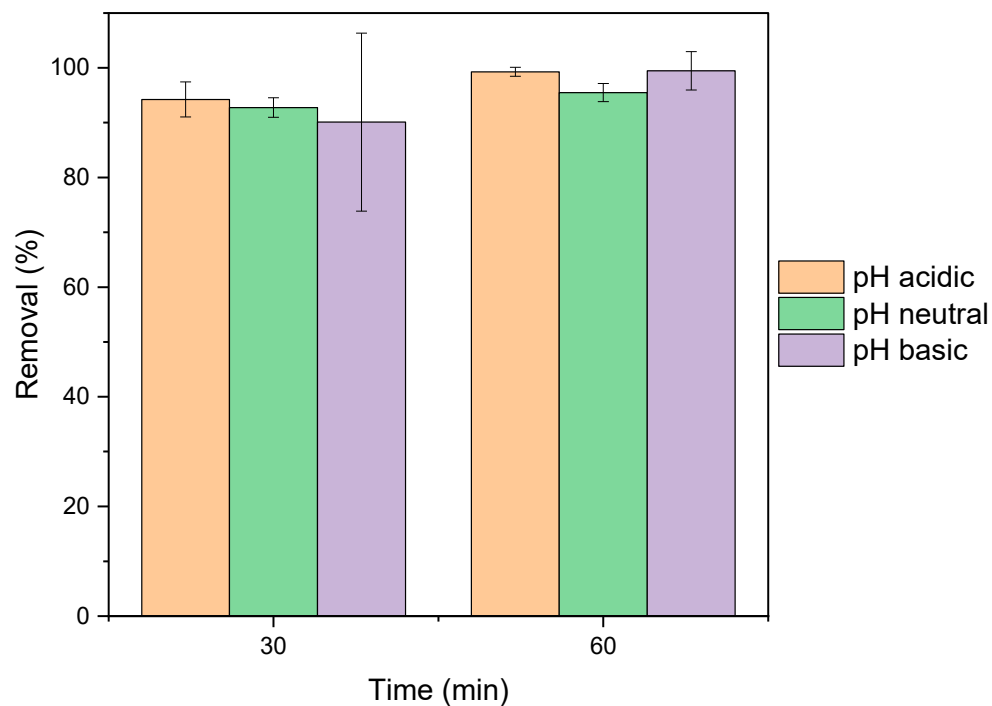


Figure 8. Effect of pH on removing NPs using Alg-C beads ($n = 3$). No significant differences were observed. The error bars represent the standard deviation of the mean calculated from triplicate experiments of each pH level.

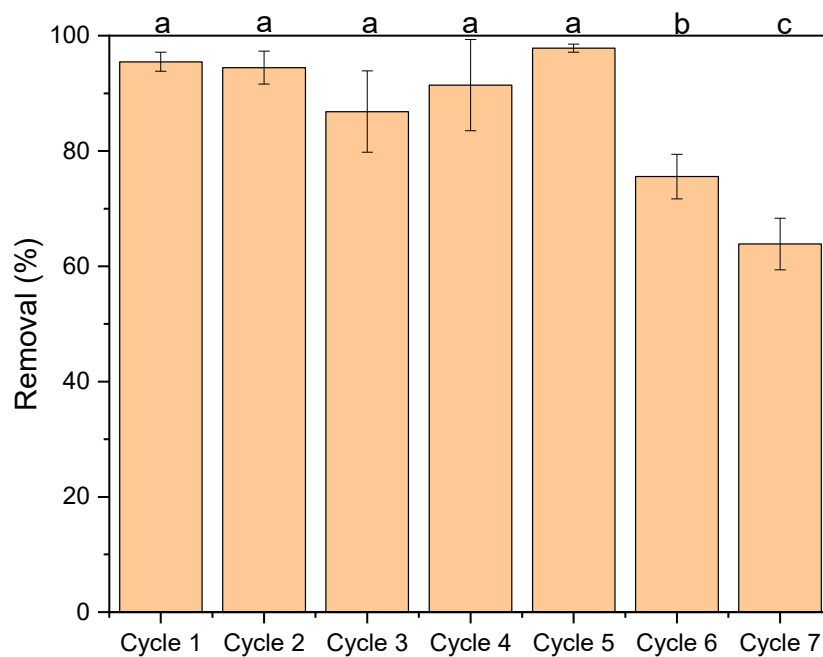


Figure 9. Reusability of Alg-C beads based on 10 mg/L (ppm) NPs at room temperature ($n = 3$). The error bars represent the standard deviation of the mean, calculated from triplicate experiments of each reusability cycle. Letters (a, b, c) are used to indicate statistically significant differences between cycles using Tukey's test ($p \leq 0.05$). Cycles with the same letter are not significantly different, while cycles with different letters are.

3.6. Wastewater Treatment

To verify the efficacy and practicality of the Alg-C beads in removing NPs, wastewater influent samples were collected from local wastewater treatment facilities. The initial analysis of NP concentration in the influent water samples revealed relatively low levels, ranging from 0.5 to 0.17 $\mu\text{g L}^{-1}$. To compare the performance of Alg-C beads in removing NPs in wastewater, assess the efficacy of Alg-C beads, and investigate potential matrix effects, additional NPs were spiked into the wastewater samples to achieve a concentration of 10 mg L^{-1} , aligning with the NP experiments in DI water performed in this study. Figure 10 illustrates the comparative effectiveness of Alg-C beads in removing NPs from both DI water samples and wastewater, showing a near-complete removal efficiency of almost 100%. These findings suggest that Alg-C beads can effectively eliminate NPs from wastewater without being significantly affected by the matrices.

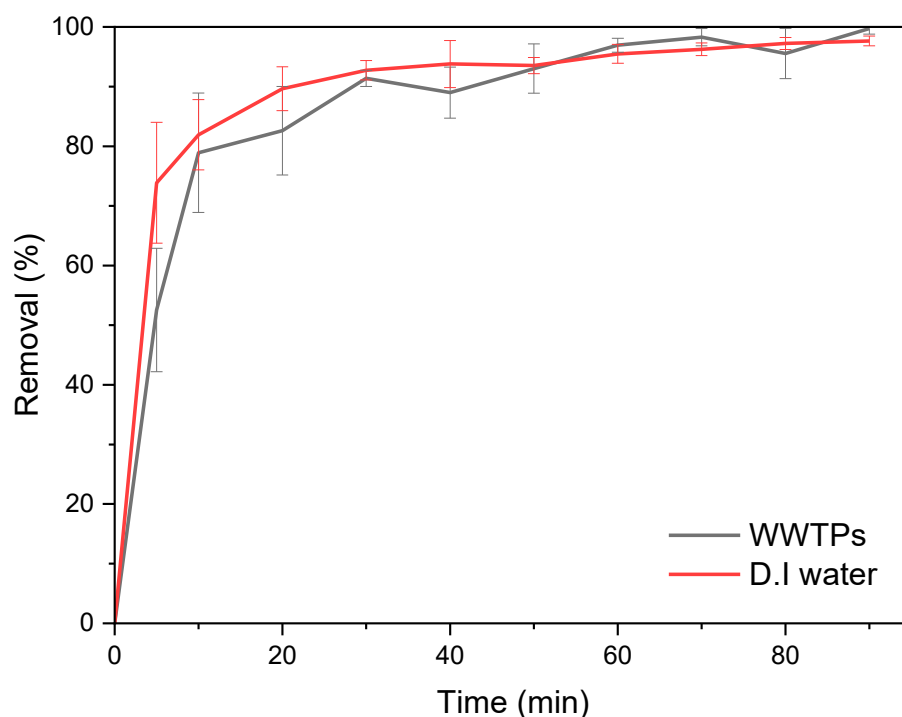


Figure 10. Removal of NPs using Alg-C beads in wastewater and water samples ($n = 3$). The error bars represent the standard deviation of each dosage level's mean, calculated from triplicate experiments of each dosage level.

These results indicate that Alg-C beads effectively remove NPs from wastewater, presenting a promising alternative. While certain bacterial strains achieve $> 90\%$ removal [50], the process may take several days. For instance, *Bacillus safensis* can degrade nearly 10 mg L^{-1} NPs over seven days [51]. Additionally, membrane filtration, particularly nanofiltration, achieves $> 90\%$ removal. Photocatalytic oxidation with UV/ TiO_2 achieves around 90% removal [4]. Notably, the Alg-C beads demonstrated 99% removal efficiency, providing a reliable NP removal option for wastewater pollution mitigation.

3.7. Comparative Analysis

Alginate-activated carbon-based materials have been reported for removing organic contaminants from water, such as methylene blue [29], diclofenac [47], paracetamol [48,52], and bisphenol-A [27], suggesting that alginate-activated carbon materials are effective and also versatile in their ability to remove a range of organic contaminants under varying conditions.

Table 7 presents a comparative study of alginate-activated carbon materials for the removal of organic contaminants in water. The table summarizes key parameters such as removal efficiency, sorbent dose, contaminant concentration, and contact time. Our study specifically evaluates the removal of nonylphenols, with removal efficiency ranging from 85.91 to 97.64%, depending on the dose and conditions used. Notably, this work achieved higher removal efficiencies compared to other studies, likely due to the higher dose of Alg-C beads (1–5 g) employed and a higher concentration of NPs (10 mg L^{−1}). Additionally, the contact time used in this work (90 min) aligns with or is shorter than the times used in other studies, further supporting the efficacy of the proposed method.

Table 7. Comparative analysis of alginate-activated carbon-based materials for organic contaminant removal in water.

	Contaminant	Removal Efficiency (%)	Sorbent Dose (g)	Contaminant Concentration (mg L ^{−1})	Contact Time (min)	Reference
1	Nonylphenols	85.9–97.6%	1–5	10	90	This work
2	Methylene blue	74.3–99.0%	0.01–0.10	50	120	[29]
3	Diclofenac	67.7–87.8%	0.02–0.25	1000	5–100	[47]
4	Paracetamol	83.6%	0.025–0.2	5–500	240	[52]
5	Bisphenol-A	~60.0–85.0%	0.1	50–500	420	[27]

4. Conclusions

This study provides insights into an eco-friendly and sustainable adsorbent material for the removal of NPs from water and wastewater. Alg-C beads were synthesized and characterized using various analytical techniques. The adsorption was optimized by evaluating key parameters, including dosage (1–5 g), contact time (90 min), adsorption capacity (0.10–0.39 mg g^{−1}), pH, and temperature, using a 10 mg L^{−1} NP solution. Isotherm and kinetic studies confirmed that the adsorption process follows the Freundlich isotherm ($R^2 = 0.96$) and second-order kinetics ($R^2 = 0.95$ to 0.99) models, suggesting a favorable interaction between NPs and Alg-C beads. Thermodynamic analysis indicated electrostatic interactions and a predominantly physical adsorption process, supported by positive Gibbs free energy and entropy change.

A key advantage of Alg-C beads is their reusability, as they maintained high removal efficiency over five cycles, reinforcing their eco-friendly potential. Overall, Alg-C beads present a promising solution for NP removal in wastewater treatment applications. This study is exploratory in nature. Our primary objective was to evaluate the effectiveness of Alg-C beads in removing nonylphenols from water and wastewater samples under static conditions, including dosage, pH, temperature, and reusability. Future studies will expand on dynamic systems and broader concentration ranges to further understand the material's capabilities.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/separations12050103/s1>, Figure S1: Example of chromatogram displaying eight distinct characteristic peaks of NPs obtained using SBSE-TDU-GS-MS analysis, Figure S2: BET surface analysis of Alg-C beads before and after interaction with NPs, illustrating changes in surface area, pore volume and distribution. The nitrogen adsorption/desorption isotherms indicate a reduced adsorbed capacity in bead's structural properties following the interaction with NPs, Figure S3: Van't Hoff plot for NPs adsorption at 4 °C (277.15 K), 21 °C (294.15 K) and 40 °C (313.15 K), Table S1: Parameters used in TDU-GC-MS for the detection of NPs.

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References

1. Sauv , S.; Desrosiers, M. A review of what is an emerging contaminant. *Chem. Cent. J.* **2014**, *8*, 15. [[CrossRef](#)] [[PubMed](#)]
2. Vasantha Raman, N.; Dubey, A.; Millar, E.; Nava, V.; Leoni, B.; Gallego, I. Monitoring contaminants of emerging concern in aquatic systems through the lens of citizen science. *Sci. Total Environ.* **2023**, *874*, 162527. [[CrossRef](#)]
3. Cantoni, B.; Ianes, J.; Bertolo, B.; Ziccardi, S.; Maffini, F.; Antonelli, M. Adsorption on activated carbon combined with ozonation for the removal of contaminants of emerging concern in drinking water. *J. Environ. Manag.* **2024**, *350*, 119537. [[CrossRef](#)]
4. Bhandari, G.; Bagheri, A.R.; Bhatt, P.; Bilal, M. Occurrence, potential ecological risks, and degradation of endocrine disrupter, nonylphenol, from the aqueous environment. *Chemosphere* **2021**, *275*, 130013. [[CrossRef](#)] [[PubMed](#)]
5. Zhao, Y.; Ji, J.; Wu, Y.; Chen, S.; Xu, M.; Cao, X.; Liu, H.; Wang, Z.; Bi, H.; Guan, G.; et al. Nonylphenol and its derivatives: Environmental distribution, treatment strategy, management and future perspectives. *Chemosphere* **2024**, *352*, 141377. [[CrossRef](#)] [[PubMed](#)]
6. Crini, G.; Cosentino, C.; Bradu, C.; Fourmentin, M.; Torri, G.; Ruzimuradov, O.; Alaton, I.A.; Tomei, M.C.; Derco, J.; Barhoumi, M.; et al. Innovative technologies to remove alkylphenols from wastewater: A review. *Environ. Chem. Lett.* **2022**, *20*, 2597–2628. [[CrossRef](#)]
7. Hong, Y.; Feng, C.; Yan, Z.; Wang, Y.; Liu, D.; Liao, W.; Bai, Y. Nonylphenol occurrence, distribution, toxicity and analytical methods in freshwater. *Environ. Chem. Lett.* **2020**, *18*, 2095–2106. [[CrossRef](#)]
8. Cheng, Q.; Du, L.; Xu, L.; Zhao, Y.; Ma, J.; Lin, H. Toxicity alleviation and metabolism enhancement of nonylphenol in green algae *Dictyosphaerium* sp. by NaHCO₃. *Sci. Total Environ.* **2022**, *848*, 157698. [[CrossRef](#)]
9. Ruczyńska, W.; Szlinder-Richert, J.; Nermer, T. The occurrence and distribution of nonylphenols and nonylphenol ethoxylates in different species of fish. *Environ. Sci. Process. Impacts* **2020**, *22*, 1057–1070. [[CrossRef](#)]
10. Wang, M.-H.; Chen, C.-F.; Albarico, F.P.J.B.; Lin, S.-L.; Chen, C.-W.; Dong, C.-D. Phthalate esters and nonylphenol concentrations correspond with microplastic distribution in anthropogenically polluted river sediments. *Mar. Pollut. Bull.* **2024**, *199*, 116031. [[CrossRef](#)]
11. Ricciardi, F.; Matozzo, V.; Marin, M.G. Effects of 4-nonylphenol exposure in mussels (*Mytilus galloprovincialis*) and crabs (*Carcinus aestuarii*) with particular emphasis on vitellogenin induction. *Mar. Pollut. Bull.* **2008**, *57*, 365–372. [[CrossRef](#)]
12. Osimitz, T.G.; Droegge, W.; Driver, J.H. Human Risk Assessment for Nonylphenol. *Hum. Ecol. Risk Assess. Int. J.* **2015**, *21*, 1903–1919. [[CrossRef](#)]
13. Nehring, I.; Staniszevska, M. Comparison of prenatal and postnatal exposure to endocrine active phenol derivatives in mammals—Humans and Baltic grey seals. *Mar. Pollut. Bull.* **2023**, *196*, 115567. [[CrossRef](#)]
14. Li, J.; Zhang, H.; Li, J.; Qin, N.; Wei, Q.; Li, Y.; Peng, Y.; Li, H. Assessment of nonylphenol exposure based on global urinary concentration data and its risk analysis. *Environ. Res.* **2024**, *244*, 117903. [[CrossRef](#)]

15. Sise, S.; Uguz, C. Nonylphenol in Human Breast Milk in Relation to Sociodemographic Variables, Diet, Obstetrics Histories and Lifestyle Habits in a Turkish Population. *Iran. J. Public Health* **2017**, *46*, 491–499. [[PubMed](#)]
16. Wang, J.; Zhang, L.; He, Y.; Ji, R. Biodegradation of phenolic pollutants and bioaugmentation strategies: A review of current knowledge and future perspectives. *J. Hazard. Mater.* **2024**, *469*, 133906. [[CrossRef](#)]
17. Weatherly, S.; Lyons, R. The photolytic conversion of 4-nonylphenol to 4-nonylcatechol within snowpack of the Palisade Glacier, Sierra Nevada, CA, USA. *Sci. Total Environ.* **2023**, *876*, 162835. [[CrossRef](#)]
18. Moukhtari, F.E.; Martín-Pozo, L.; Zafra-Gómez, A. Strategies based on the use of microorganisms for the elimination of pollutants with endocrine-disrupting activity in the environment. *J. Environ. Chem. Eng.* **2023**, *11*, 109268. [[CrossRef](#)]
19. Ho, H.; Watanabe, T. Distribution and Removal of Nonylphenol Ethoxylates and Nonylphenol from Textile Wastewater—A Comparison of a Cotton and a Synthetic Fiber Factory in Vietnam. *Water* **2017**, *9*, 386. [[CrossRef](#)]
20. Arifin, M.N.; Jusoh, R.; Abdullah, H.; Ainirazali, N.; Setiabudi, H.D. Recent advances in advanced oxidation processes (AOPs) for the treatment of nitro- and alkyl-phenolic compounds. *Environ. Res.* **2023**, *229*, 115936. [[CrossRef](#)]
21. Zhang, Y.; Zhang, X.; Wang, S. Recent advances in the removal of emerging contaminants from water by novel molecularly imprinted materials in advanced oxidation processes—A review. *Sci. Total Environ.* **2023**, *883*, 163702. [[CrossRef](#)]
22. Yan, X.; Zhang, Q.; Rao, Q.; Chen, S.; Wang, X.; Song, W.; Cheng, L.; Guan, S.; Song, W. Efficient Removal of Nonylphenol Contamination from Water Using Optimized Magnesium Silicate. *Materials* **2022**, *15*, 4445. [[CrossRef](#)] [[PubMed](#)]
23. Hassan, A.F.; Abdel-Mohsen, A.M.; Fouda, M.M.G. Comparative study of calcium alginate, activated carbon, and their composite beads on methylene blue adsorption. *Carbohydr. Polym.* **2014**, *102*, 192–198. [[CrossRef](#)]
24. Sinha, P.; Banerjee, S.; Kar, K.K. Characteristics of Activated Carbon. In *Handbook of Nanocomposite Supercapacitor Materials I*; Kar, K.K., Ed.; Springer Series in Materials Science; Springer International Publishing: Cham, Switzerland, 2020; Volume 300, pp. 125–154, ISBN 978-3-030-43008-5.
25. Quesada, H.B.; De Araújo, T.P.; Vareschini, D.T.; De Barros, M.A.S.D.; Gomes, R.G.; Bergamasco, R. Chitosan, alginate and other macromolecules as activated carbon immobilizing agents: A review on composite adsorbents for the removal of water contaminants. *Int. J. Biol. Macromol.* **2020**, *164*, 2535–2549. [[CrossRef](#)]
26. Sher, F.; Hanif, K.; Rafey, A.; Khalid, U.; Zafar, A.; Ameen, M.; Lima, E.C. Removal of micropollutants from municipal wastewater using different types of activated carbons. *J. Environ. Manag.* **2021**, *278*, 111302. [[CrossRef](#)]
27. Fuzil, N.S.; Othman, N.H.; Jamal, N.A.S.R.A.; Mustapa, A.N.; Alias, N.H.; Dollah, 'A.; Him, N.R.N.; Marpani, F. Bisphenol A Adsorption from Aqueous Solution Using Graphene Oxide-Alginate Beads. *J. Polym. Environ.* **2022**, *30*, 597–612. [[CrossRef](#)]
28. Lee, J.W.; Han, J.; Choi, Y.-K.; Park, S.; Lee, S.H. Reswellable alginate/activated carbon/carboxymethyl cellulose hydrogel beads for ibuprofen adsorption from aqueous solutions. *Int. J. Biol. Macromol.* **2023**, *249*, 126053. [[CrossRef](#)]
29. Nasrullah, A.; Bhat, A.H.; Naeem, A.; Isa, M.H.; Danish, M. High surface area mesoporous activated carbon-alginate beads for efficient removal of methylene blue. *Int. J. Biol. Macromol.* **2018**, *107*, 1792–1799. [[CrossRef](#)]
30. Kumar, A.; Prasad, B.; Mishra, I.M. Isotherm and kinetics study for acrylic acid removal using powdered activated carbon. *J. Hazard. Mater.* **2010**, *176*, 774–783. [[CrossRef](#)]
31. Omer, A.M.; Abdel-Alim Sadik, W.; Elady, R.A.; Tamer, T.M.; Abd-Ellatif, M.M.; Mohy-Eldin, M.S. Novel amino-ethyl carboxymethyl cellulose crosslinked ampholyte hydrogel development for Methyl Orange Removal from Waste water: Kinetics, isotherms, and thermodynamics studies. *Desalination Water Treat.* **2024**, *317*, 100041. [[CrossRef](#)]
32. Khedr, A.A.; Fawzy, M.E.; Ahmed, H.M.; Alshammari, S.O.; El-Khateeb, M.A. Treatment of heavy metal ions from simulated water using adsorption process via modified iron magnetic nanocomposite. *Desalination Water Treat.* **2024**, *317*, 100071. [[CrossRef](#)]
33. Kwak, H.W.; Hong, Y.; Lee, M.E.; Jin, H.-J. Sericin-derived activated carbon-loaded alginate bead: An effective and recyclable natural polymer-based adsorbent for methylene blue removal. *Int. J. Biol. Macromol.* **2018**, *120*, 906–914. [[CrossRef](#)] [[PubMed](#)]
34. Pathania, D.; Sharma, S.; Singh, P. Removal of methylene blue by adsorption onto activated carbon developed from Ficus carica bast. *Arab. J. Chem.* **2017**, *10*, S1445–S1451. [[CrossRef](#)]
35. Balsiger, H.A.; De La Torre, R.; Lee, W.-Y.; Cox, M.B. A four-hour yeast bioassay for the direct measure of estrogenic activity in wastewater without sample extraction, concentration, or sterilization. *Sci. Total Environ.* **2010**, *408*, 1422–1429. [[CrossRef](#)]
36. Alamin, N.U.; Khan, A.S.; Nasrullah, A.; Iqbal, J.; Ullah, Z.; Din, I.U.; Muhammad, N.; Khan, S.Z. Activated carbon-alginate beads impregnated with surfactant as sustainable adsorbent for efficient removal of methylene blue. *Int. J. Biol. Macromol.* **2021**, *176*, 233–243. [[CrossRef](#)]
37. Park, H.G.; Kim, T.W.; Chae, M.Y.; Yoo, I.-K. Activated carbon-containing alginate adsorbent for the simultaneous removal of heavy metals and toxic organics. *Process Biochem.* **2007**, *42*, 1371–1377. [[CrossRef](#)]
38. De Araújo, T.P.; Quesada, H.B.; Dos Santos, D.F.; Da Silva Fonseca, B.C.; Barbieri, J.Z.; Bergamasco, R.; De Barros, M.A.S.D. Acetaminophen removal by calcium alginate/activated hydrochar composite beads: Batch and fixed-bed studies. *Int. J. Biol. Macromol.* **2022**, *203*, 553–562. [[CrossRef](#)]

39. Khan, A.S.; Ibrahim, T.H.; Khamis, M.I.; Nancarrow, P.; Iqbal, J.; AlNashef, I.; Jabbar, N.A.; Hassan, M.F.; Mjalli, F.S. Preparation of sustainable activated carbon-alginate beads impregnated with ionic liquid for phenol decontamination. *J. Clean. Prod.* **2021**, *321*, 128899. [\[CrossRef\]](#)
40. Sujiono, E.H.; Zabrian, D.; Zurnansyah; Mulyati; Zharvan, V.; Samnur; Humairah, N.A. Fabrication and characterization of coconut shell activated carbon using variation chemical activation for wastewater treatment application. *Results Chem.* **2022**, *4*, 100291. [\[CrossRef\]](#)
41. Wang, B.; Wan, Y.; Zheng, Y.; Lee, X.; Liu, T.; Yu, Z.; Huang, J.; Ok, Y.S.; Chen, J.; Gao, B. Alginate-based composites for environmental applications: A critical review. *Crit. Rev. Environ. Sci. Technol.* **2019**, *49*, 318–356. [\[CrossRef\]](#)
42. Shamsudin, M.S.; Azha, S.F.; Sellaoui, L.; Badawi, M.; Bonilla-Petriciolet, A.; Ismail, S. Performance and interactions of diclofenac adsorption using Alginate/Carbon-based Films: Experimental investigation and statistical physics modelling. *Chem. Eng. J.* **2022**, *428*, 131929. [\[CrossRef\]](#)
43. Kalam, S.; Abu-Khamsin, S.A.; Kamal, M.S.; Patil, S. Surfactant Adsorption Isotherms: A Review. *ACS Omega* **2021**, *6*, 32342–32348. [\[CrossRef\]](#)
44. Tang, Y.; Liu, D.; He, H.; Zou, J.; Wang, D.; Yang, X.; Zhang, L.; Yang, C. Immobilization of zirconium-modified activated carbon in an alginate matrix for the removal of atrazine: Preparation, performances and mechanisms. *Environ. Technol. Innov.* **2024**, *35*, 103699. [\[CrossRef\]](#)
45. Sun, R.; Gao, S.; Zhang, K.; Cheng, W.-T.; Hu, G. Recent advances in alginate-based composite gel spheres for removal of heavy metals. *Int. J. Biol. Macromol.* **2024**, *268*, 131853. [\[CrossRef\]](#) [\[PubMed\]](#)
46. Raghav, S.; Kumar, D. Adsorption Equilibrium, Kinetics, and Thermodynamic Studies of Fluoride Adsorbed by Tetrametallic Oxide Adsorbent. *J. Chem. Eng. Data* **2018**, *63*, 1682–1697. [\[CrossRef\]](#)
47. Al-Hazmi, G.A.A.M.; Alayyafi, A.A.; El-Desouky, M.G.; El-Bindary, A.A. Guava seed activated carbon loaded calcium alginate aerogel for the adsorption of diclofenac sodium: Characterization, isotherm, kinetics, and optimization via Box-Behnken design. *Int. J. Biol. Macromol.* **2024**, *262*, 129995. [\[CrossRef\]](#) [\[PubMed\]](#)
48. Mahmoud, R.; Mahgoub, S.M.; Ashraf, A.M.; Allam, A.A.; Alawam, A.S.; Rudayni, H.A.; Moaty, S.A. Activated carbon alginate as adsorbent for simultaneous removal of almotriptan and paracetamol from binary solutions. *Sustain. Chem. Pharm.* **2024**, *41*, 101708. [\[CrossRef\]](#)
49. Chaima, H.; Eddine, B.C.; Faouzia, B.; Rana, H.; Aymene Salah, B.; Gil, A.; Imene, B.-A.; Ferhat, D.; Riadh, B.; Mokhtar, B. Adsorptive removal of cationic dye from aqueous solutions using activated carbon prepared from *Crataegus monogyna*/sodium alginate/polyaniline composite beads: Experimental study and molecular dynamic simulation. *J. Mol. Liq.* **2024**, *408*, 125372. [\[CrossRef\]](#)
50. Liu, Z.; Kanjo, Y.; Mizutani, S. Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment—Physical means, biodegradation, and chemical advanced oxidation: A review. *Sci. Total Environ.* **2009**, *407*, 731–748. [\[CrossRef\]](#)
51. Lara-Moreno, A.; Aguilar-Romero, I.; Rubio-Bellido, M.; Madrid, F.; Villaverde, J.; Santos, J.L.; Alonso, E.; Morillo, E. Novel nonylphenol-degrading bacterial strains isolated from sewage sludge: Application in bioremediation of sludge. *Sci. Total Environ.* **2022**, *847*, 157647. [\[CrossRef\]](#)
52. Mahgoub, S.M.; Kotp, A.A.; Mohamed, M.A.; Alfassam, H.E.; Rudayni, H.A.; Allam, A.A.; Mahmoud, R.; Abdel Moaty, S.A. Assessment of activated carbon/alginate for the concurrent removal efficiency of paracetamol and caffeine from wastewater in their binary solutions. *Chin. J. Anal. Chem.* **2024**, *52*, 100403. [\[CrossRef\]](#)

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