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Research Article

Adsorption capacity of groundnut husk based activated carbon for removal of urea from aqueous solution

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ABSTRACT

Nitrogenous pollutants, such as urea, significantly contribute to water contamination and eutrophication. Low-cost, sustainable adsorbents derived from agricultural wastes have shown promise in removing these compounds. Groundnut husk, an abundant biomass, was investigated as a precursor for activated carbon (GHAC) to assess its efficiency in urea adsorption from aqueous solutions. A total of 200 g of groundnut husks were thoroughly washed with distilled water to remove dirt and other impurities. The cleaned husks were then dried in an oven at 120 °C to eliminate moisture. This study aimed to evaluate GHAC for urea removal, examining the effects of adsorbent dosage, pH, contact time, and initial urea concentration on adsorption performance. Batch adsorption experiments revealed that GHAC achieved optimal adsorption at 0.8 g dosage with a maximum capacity of 9.48 mg/g. Adsorption was highly pH-dependent, peaking at pH 0.9, Contact time studies showed rapid adsorption, with equilibrium reached within 30 minutes. Increasing initial urea concentrations enhanced adsorption, indicating strong pore accessibility and high affinity of GHAC. Isotherm analyses revealed that the Freundlich model best described the adsorption, suggesting heterogeneous, multilayer coverage. Kinetic studies indicated that pseudo-second-order kinetics predominated, signifying chemisorption as the main mechanism. GHAC is an effective, low-cost, and environmentally friendly adsorbent for urea removal, demonstrating rapid kinetics, high adsorption capacity, and favorable surface interactions suitable for wastewater treatment applications. Optimization studies where carried out to determine the optimum conditions for carbon dosage, pH and contact time removal of Urea from wastewater. Future studies should explore chemical surface modification, application to real wastewater, thermodynamic characterization, regeneration and reusability, development of hybrid adsorbent systems, structural analysis, and column-scale experiments to optimize industrial-scale application. The study convincingly demonstrates that GHAC is an efficient, inexpensive, and environmentally friendly adsorbent suitable for removing urea from contaminated water

Keywords: Groundnut husk, Activated carbon, Urea removal, Adsorption, Isotherms, Kinetics, Chemisorption

Introduction

Activated carbon is a highly porous, microcrystalline form of black carbonaceous material that is non-graphitic in nature and distinguished by its remarkable physical and chemical properties. Its extensive surface area, significant microporosity, high adsorption capacity, and surface reactivity enable it to interact effectively with a wide range of chemical species, making it indispensable in industrial and environmental applications (Hashem et al., 2024; McCaffrey et al., 2024). These unique properties allow activated carbon to trap and retain contaminants from gases, liquids, and solutions, supporting purification, separation, and remediation processes across multiple sectors. The versatility of activated carbon is reflected in its applications across industries such as chemical manufacturing, food processing, wastewater treatment, air pollution control, and hydrometallurgy, including the recovery of precious metals like gold and silver. Its ability to -

selectively adsorb molecules based on size, polarity, and chemical affinity ensures effectiveness under diverse operational conditions while its reusability enhances its economic and industrial value (Adewuji et al., 2021).

In recent years, there has been growing interest in producing activated carbon from agricultural by-products due to their environmental and economic advantages over conventional coal-based or mineral-derived carbons. Agricultural residues, which would otherwise be considered waste, provide a renewable and sustainable source of raw materials while reducing the environmental impact of waste accumulation (McCaffrey et al., 2024). These residues, including coconut shells, almond shells, palm shells, sugarcane bagasse, corn cobs, groundnut shells, and rice bran, have demonstrated adsorption efficiencies comparable to or exceeding those of traditional activated carbons (McCaffrey et al., 2024). The utilization of such waste not only supports environmental sustainability but also offers cost-effective alternatives for industries, particularly in developing countries where agricultural residues are abundant and often underutilized. This approach aligns with principles of waste valorization and circular economy, transforming potential pollutants into valuable industrial products.

Groundnut shells, in particular, have been identified as a promising precursor for activated carbon production due to their widespread availability in northern Nigeria, where over 80 tonnes of shell waste are generated annually. Left unmanaged, these residues pose environmental and public health challenges, as they can harbor rodents and mosquitoes, leading to disease risks (Amin et al., 2019). Converting groundnut shells into activated carbon not only provides an effective method of waste management but also creates a commercially useful product with high adsorption potential. The process typically involves carbonization, which increases carbon content and develops initial porosity, followed by activation, which enhances pore structure, surface area, and chemical functionalities. Activation can be carried out through physical methods, such as controlled heating under inert conditions, or chemical methods, using acids, bases, or salts to optimize adsorption performance (Adewuji et al., 2021).

The transformation of agricultural residues into activated carbon produces materials with well-defined micro-, meso-, and macroporous structures, critical for high adsorption efficiency. A hierarchical pore structure provides increased surface area and more accessible adsorption sites, enabling the carbon to retain molecules effectively across a range of industrial, environmental, and analytical applications (Adewuji et al., 2021). Careful control of precursor selection, activation methods, and operating conditions allows the production of activated carbon tailored to specific applications, demonstrating its adaptability and industrial relevance. Local production of activated carbon from groundnut shells addresses the dual challenges of agricultural waste management and the high cost of imported carbon, providing industries with a reliable, affordable, and environmentally sustainable material.

This study is therefore significant for economic, environmental, and social reasons. Economically, producing activated carbon locally reduces dependence on costly imports and supports the development of small- and medium-scale enterprises focused on agricultural by-products. Environmentally, it mitigates the hazards associated with agricultural waste, preventing soil and water pollution while reducing disease vector proliferation. Socially, it improves public health by reducing unsanitary waste accumulation and promotes community engagement in sustainable practices. By focusing specifically on groundnut shells, the study provides a practical and scalable approach to converting a readily available agricultural residue into a valuable industrial material. This work highlights the potential of integrating waste valorization into industrial processes, reflecting the principles of sustainability, circular economy, and responsible resource utilization.

Material and Methods

Materials

The primary materials used in this study included groundnut husks, which served as the raw material for producing activated carbon, and sulfuric acid (H_2SO_4) employed as the chemical activating agent. Distilled water was utilized for washing and purification steps, while barium chloride ($BaCl_2$) solution was applied to verify the complete removal of residual sulfate ions. The apparatus used comprised an oven for drying, a muffle furnace for final carbon activation, and sieves to obtain particles of uniform size ranging from 20 - 40 mesh.

For the urea adsorption experiments, urea acted as the adsorbate, while the chemicals required for its quantification using the diacetyl monoxime (DAM) colorimetric method included diacetyl monoxime, acidic ferric chloride solution, and thiosemicarbazide solution. Additional reagents, such as dilute hydrochloric acid (HCl) and sodium hydroxide (NaOH), were used to adjust the pH of solutions. Analytical measurements were conducted using a spectrophotometer, and laboratory glassware including pipettes, volumetric flasks, and test tubes were employed throughout the experimental procedures.

Preparation of Activated Carbon from Groundnut Husks

Activated carbon was synthesized from groundnut husks through chemical activation using concentrated sulfuric acid. The process began with the collection and preparation of the raw material.

A total of 200 g of groundnut husks were thoroughly washed with distilled water to remove dirt and other impurities. The cleaned husks were then dried in an oven at 120 °C to eliminate moisture. For the activation step, the dried husks were impregnated with concentrated H_2SO_4 and subsequently returned to the oven for carbonization at 160 °C for 24 hours (Amin *et al*., 2019).

The resulting carbonaceous char was washed repeatedly with distilled water to remove residual acid. The efficiency of the washing process was confirmed using $BaCl_2$ solution; the absence of a precipitate indicated complete removal of sulfate

ions. The purified carbon was dried at 110 °C and sieved to isolate particles within the 20 - 40 mesh range. Final activation was carried out in a muffle furnace at 200 °C for three hours. The activated carbon produced was stored in a desiccator to prevent moisture absorption prior to its application in adsorption experiments (Amin *et al*., 2019).

Analytical Determination of Urea

The concentration of urea in aqueous solutions was determined using the diacetyl monoxime (DAM) colorimetric method, which forms a colored complex in the presence of urea.

Preparation of Reagents

Analytical reagents for urea quantification were prepared as follows: A 0.2% DAM solution was made by dissolving 0.20 g of diacetyl monoxime in 100 mL of distilled water, with gentle mixing until completely dissolved. The solution was stored in an amber container to protect it from light.

The acidic ferric chloride reagent was prepared by dissolving 0.81 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in 50 mL of distilled water to make a 0.05 M solution. Separately, 10 mL of concentrated H_2SO_4 was diluted to 100 mL with distilled water in an ice bath to achieve a 10% acidic medium. The ferric chloride solution was then added slowly to the acid with constant stirring to produce a uniform acidic ferric chloride reagent. A 0.02% thiosemicarbazide solution was prepared by dissolving 0.02 g of thiosemicarbazide in 100 mL of distilled water and stored in a glass-stoppered container (Saeed & Al-Fatemi, 2018).

For calibration, a stock urea solution of 1000 mg/L was prepared by dissolving 1.00 g of analytical-grade urea in 1 L of distilled water. Working standards of 20, 40, 60, 80, and 100 mg/L were obtained by diluting 2, 4, 6, 8, and 10 mL of the stock solution to 100 mL with distilled water in volumetric flasks. Each solution was mixed thoroughly to ensure homogeneity before use in constructing a calibration curve.

Determination of Urea in Samples

For both standard and unknown solutions, 2 mL of the sample was transferred into a test tube, followed by the sequential addition of 2 mL DAM reagent, 1 mL acidic ferric chloride, and 1 mL thiosemicarbazide solution. The mixture was mixed thoroughly and heated in a boiling water bath at ~100°C for 10 minutes to allow color development. After cooling to room temperature, the absorbance of the resulting colored complex was measured at 520 nm using a spectrophotometer. The calibration curve obtained from standard solutions was used to calculate the urea concentration in unknown samples based on their measured absorbance.

Experimental Design for Adsorption Studies

The adsorption behavior of the prepared activated carbon was examined through a structured set of batch experiments aimed at optimizing key operational parameters. To maintain consistency in reporting, the impregnation ratio (IR) defined as the mass of urea per mass of precursor was adopted. For a standard 5.00 g batch of groundnut husk precursor, the corresponding IR values for urea amounts ranging from 0.10 g to 1.00 g were calculated and are summarized in Table 3.1.

Table 1. Standardized Urea Impregnation Ratios for a 5.00 g Precursor Batch

Urea (g)	Moles urea (mol)	Molarity in 20 mL solution (M)	Impregnation ratio IR = urea/precursor (g/g)
0.10	0.001665	0.0833	0.0200
0.20	0.003330	0.1665	0.0400
0.40	0.006660	0.3330	0.0800
0.60	0.009990	0.4995	0.1200
0.80	0.013320	0.6660	0.1600
1.00	0.016650	0.8325	0.2000

The effect of adsorbent dosage was explored by altering the quantity of activated carbon added to a fixed volume of urea solution with a set initial concentration. The objective was to determine the optimal adsorbent mass that maximizes urea removal efficiency while maintaining a satisfactory adsorption capacity per unit mass (q_e). Typically, increasing the adsorbent mass enhances the removal percentage, but it can reduce the specific adsorption capacity due to site saturation or particle aggregation.

The influence of solution pH on adsorption was investigated by adjusting the urea solution pH across a range of 2 to 10, using dilute sodium hydroxide (NaOH) or hydrochloric acid (HCl). Solution pH is a vital parameter, as it affects both the surface charge of the activated carbon and the ionic form of urea, thereby controlling the electrostatic interactions responsible for the adsorption process.

Adsorption kinetics were studied to examine the time-dependent behavior of urea uptake. A known mass of activated carbon was stirred with the urea solution, and samples were collected at defined time intervals. The urea concentration at each interval was measured to calculate the amount adsorbed at time t (q_t). The data were then fitted to kinetic models, such as pseudo-first-order and pseudo-second-order, to identify the rate-determining steps and clarify the adsorption mechanism. The contact time required to reach equilibrium was determined and used in subsequent equilibrium studies.

Finally, adsorption isotherms at equilibrium were established by contacting a fixed mass of activated carbon with urea solutions of varying initial concentrations until equilibrium was attained. The equilibrium data, expressed as the concentration of urea in solution at equilibrium (C_e) versus the corresponding solid-phase loading (q_e), were analyzed using widely accepted models, including Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherms, to determine the maximum adsorption capacity and gain insight into surface characteristics and adsorption energetics.

Results

Effect of Adsorbent Dosage on Urea Adsorption

Adsorbent dosage plays a crucial role in urea adsorption because it determines the number of active sites available for solute uptake. In this study, the adsorption capacity (qe) increased

from 9.22 mg/g at 0.2 g to a maximum of 9.48 mg/g at 0.8 g, after which it declined to 2.97 mg/g at 2.0 g. At low dosages, the relatively high concentration of urea per gram of adsorbent allows efficient occupation of active sites, resulting in higher adsorption capacity. However, as the dosage increases, overcrowding or particle agglomeration reduces the effective surface area, limiting access to internal pores (Foo & Hameed, 2010). Beyond the optimal dosage, the low solute-to-adsorbent ratio causes many active sites to remain unoccupied, producing a dilution effect that decreases qe. Similar trends have been reported for other biomass-derived carbons, such as palm kernel shell (Ajayi & Adebayo, 2013) and rice husk carbon (Gimba *et al*., 2016), highlighting that moderate dosages achieve the best balance between active site availability and solute concentration. Consequently, 0.8 g was identified as the optimal dosage for GHAC in this study.

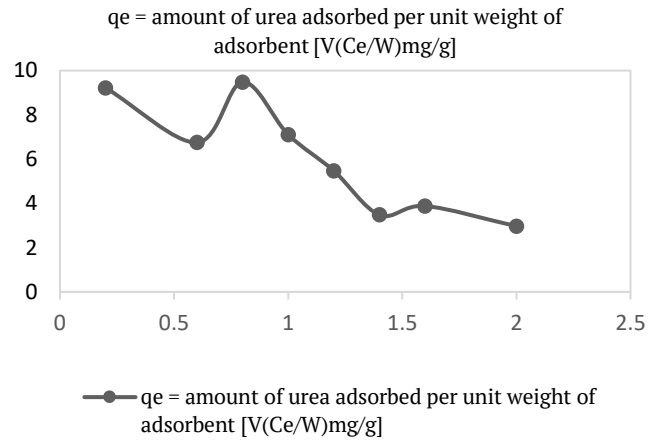


Figure 1. Data for the effective activated carbon (adsorbent) dosage on the adsorption of Urea (adsorbate) from aqueous solution.

Effect of pH on Urea Adsorption

The pH of the solution significantly affects the adsorption of urea on GHAC by influencing both the adsorbent's surface chemistry and the ionization state of urea. Adsorption capacity increased from 2.31 mg/g at very low pH (0.2) to a maximum of 9.85 mg/g at the optimal pH of 0.9, after which it declined at higher pH values. At mildly acidic conditions, the moderately protonated carbon surface promotes strong hydrogen bonding, dipole–dipole, and weak donor–acceptor interactions with urea's carbonyl and amine groups, enhancing adsorption. Extremely low pH leads to competition between excess H^+ ions and urea for active sites, while higher pH reduces surface protonation, weakening binding interactions and decreasing adsorption efficiency. These trends align with previous studies, which report that optimal urea uptake occurs in mildly acidic environments due to favorable surface charge interactions and enhanced binding with nitrogen-containing compounds (Amin *et al*., 2019; Samarghandi *et al*., 2011).

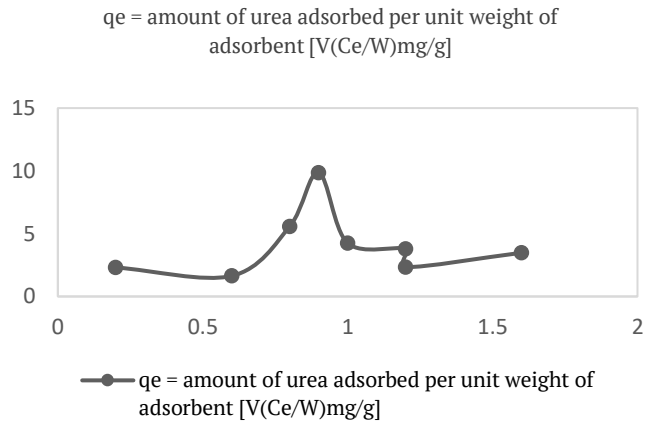


Figure 2. Data for the effects of pH on the adsorption of Urea from aqueous solution

Effect of Contact Time on Urea Adsorption

The adsorption of urea onto GHAC was strongly time-dependent, with uptake increasing rapidly from 9.39 mg/g at 5 minutes to a maximum of 17.09 mg/g at 30 minutes, followed by a slight decline. The initial fast adsorption phase is attributed to the abundance of accessible surface sites, allowing urea molecules to bind quickly with minimal diffusion resistance. Over time, adsorption slows as urea penetrates the micro-pores in an intraparticle diffusion stage, limited by pore diffusion. The slight decrease after 30 minutes suggests that dynamic equilibrium is approached, with adsorption and desorption rates balancing or minor desorption occurring from weakly bound urea. These results are consistent with previous studies on agricultural carbons, such as those by Hameed and El-Khaiary (2008) and Abdulraheem *et al*. (2014), which reported rapid initial uptake and equilibrium within a short time due to the highly porous structure of bio-derived adsorbents.

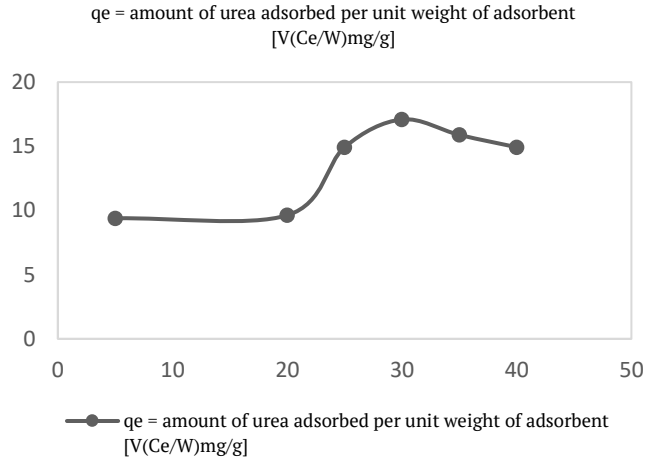


Figure 3. Data for the effects of contact time on the adsorption of Urea from aqueous solution

Effect of Initial Urea Concentration

The adsorption of urea onto GHAC increased steadily with rising initial concentrations, from 100.70 mg/L at 130 mg/L to 802.98 mg/L at 900 mg/L, due to an enhanced mass transfer driving force that promotes interactions between urea molecules and the adsorbent surface. This trend reflects the high capacity of GHAC to accommodate significant urea loads, attributed to its accessible micro- and meso-pores capable of supporting multilayer adsorption. The absence of saturation within the tested range indicates a complex pore structure and broad pore size distribution, consistent with findings by Ayawei et al. (2015) and Saeed & Al-Fatemi (2018), who observed similar increases in adsorption with higher initial concentrations. These results suggest that GHAC is an effective adsorbent for industrial and agricultural wastewater containing high levels of nitrogenous pollutants.

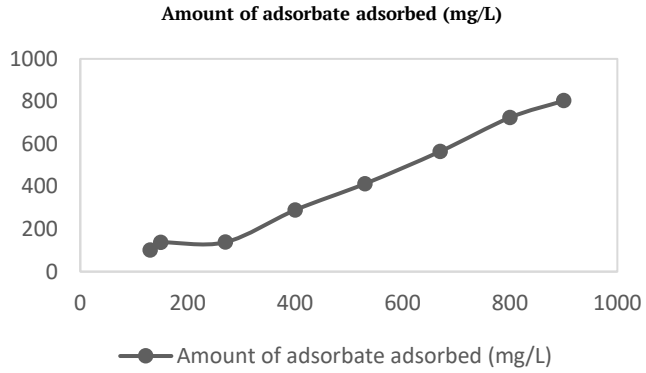


Figure 4. Data for the effects of adsorbate dosage on the adsorption of Urea from aqueous solution

Langmuir Isotherm

The adsorption of urea onto groundnut husk–based activated carbon (GHAC) was evaluated using the Langmuir isotherm, which assumes monolayer adsorption on a homogeneous surface without interactions between adsorbed molecules (Langmuir, 1918). The linear plot of Ce/qe versus Ce demonstrated near-linearity, indicating that adsorption occurs primarily as a monolayer on the GHAC surface. The high qe values (12.59–17.26 mg/g) reflect strong interactions between urea molecules and the available active sites, while the increase in Ce/qe at higher concentrations suggests that the surface approaches saturation. These results align with previous studies on agricultural-waste carbons, confirming that biosorbents with well-developed microporous surfaces often exhibit Langmuir-type adsorption behavior (Boudrahem et al., 2017; Singh & Uma, 2020; Bello & Ahmad, 2017).

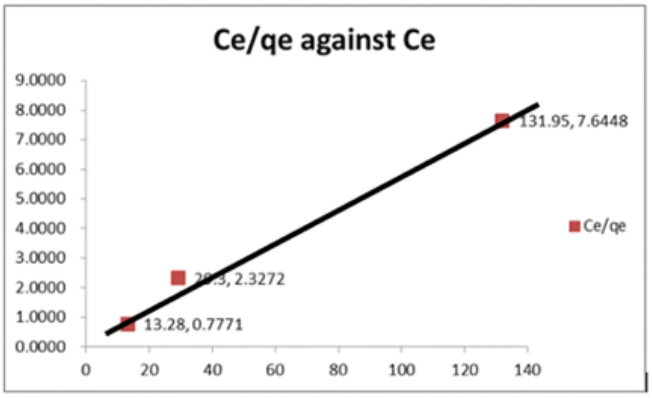


Figure 5. Langmuir model plotting Ce/qe against Ce

Freundlich Isotherm

The Freundlich isotherm was applied to account for heterogeneous adsorption sites and surface energy variations, described empirically by the log qe versus log Ce relationship (Negi & Anmd, 2007). The linearity of the plot confirmed that urea adsorption onto GHAC increased proportionally with concentration, indicating favorable adsorption on a non-uniform surface. The adsorption intensity ($1/n < 1$) suggests good affinity between urea and the biosorbent, reflecting the presence of varying pore sizes and functional groups on the activated carbon. This behavior is consistent with reports on plant-based carbons for nitrogenous compound removal, emphasizing the heterogeneous nature of adsorption in biomass-derived carbons (Adewuyi et al., 2021; Ibisi & Nwabanne, 2017).

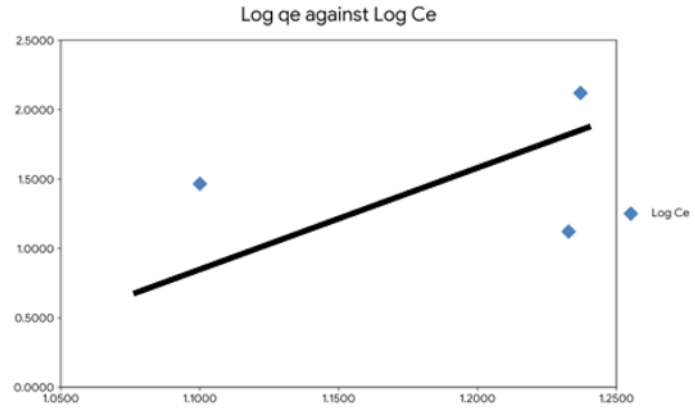


Figure 6. Freudlich model plotting Log qe against Log Ce

Temkin Isotherm

The Temkin isotherm model accounts for adsorbate–adsorbent interactions and assumes that the heat of adsorption decreases linearly with surface coverage (Temkin & Pyzhev, 1940). The linear relationship observed when plotting qe against ln Ce indicated moderate B values, implying that adsorption is influenced mainly by weak intermolecular forces characteristic of physisorption. The decreasing heat of adsorption with increased coverage reflects energetic diversity among active sites, which is typical of biomass-derived activated carbon.

These findings suggest that GHAC provides a variety of adsorption energies, consistent with studies on urea and nitrogenous compound adsorption (Auta & Hameed, 2014).

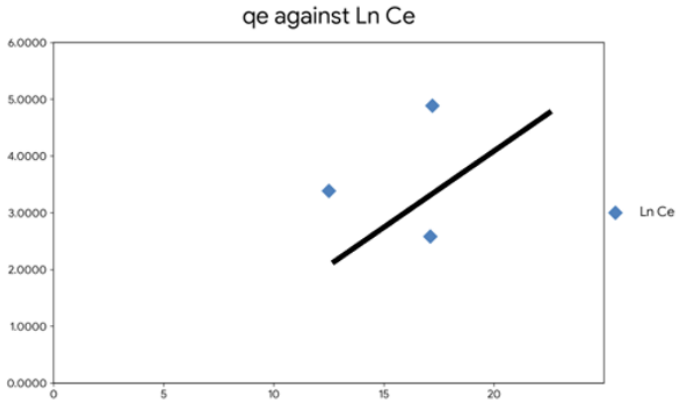


Figure 7. Temkim model plotting qe against Ln Ce

Dubinin–Radushkevich (D–R) Isotherm

The D–R isotherm was used to estimate adsorption energy and distinguish between physical and chemical adsorption. Calculations based on $1/qe^2$ values revealed low adsorption energy ($E < 8$ kJ/mol), indicating that urea adsorption onto GHAC is dominated by physisorption mechanisms such as van der Waals forces, hydrogen bonding, and weak surface polarization. This result aligns with previous studies on nitrogen compound adsorption using coconut-shell and palm-kernel carbons (Ho & McKay, 1999; Bello & Ahmad, 2017), confirming that GHAC primarily relies on physical interactions for urea uptake.

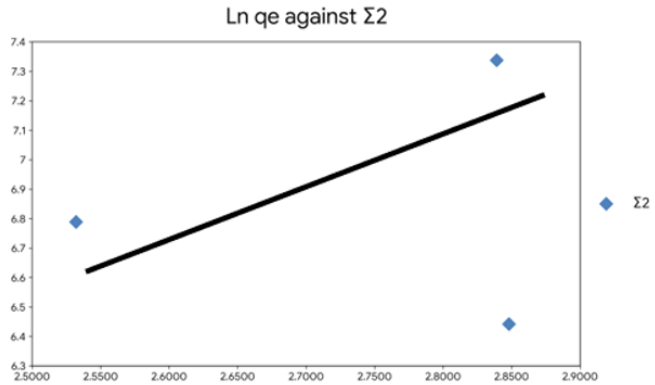


Figure 8. DKR model plotting Ln qe against ∑2

Adsorption Kinetics

Kinetic studies of urea adsorption onto GHAC indicated that the pseudo-first-order model poorly described the process, suggesting that physical adsorption alone was insufficient to explain the adsorption rate. In contrast, the pseudo-second-order model showed strong agreement, indicating that the rate-limiting step involves chemisorption through hydrogen bonding or electron-sharing between urea and oxygenated functional groups on GHAC. This behavior suggests that both physical and chemical mechanisms contribute to adsorption, with chemisorption playing a significant role. Similar kinetic patterns have been reported in studies on biomass-derived activated carbons for nitrogenous compounds (Ho & McKay, 1999; Saeed et al., 2015; Bello & Ahmad, 2012).

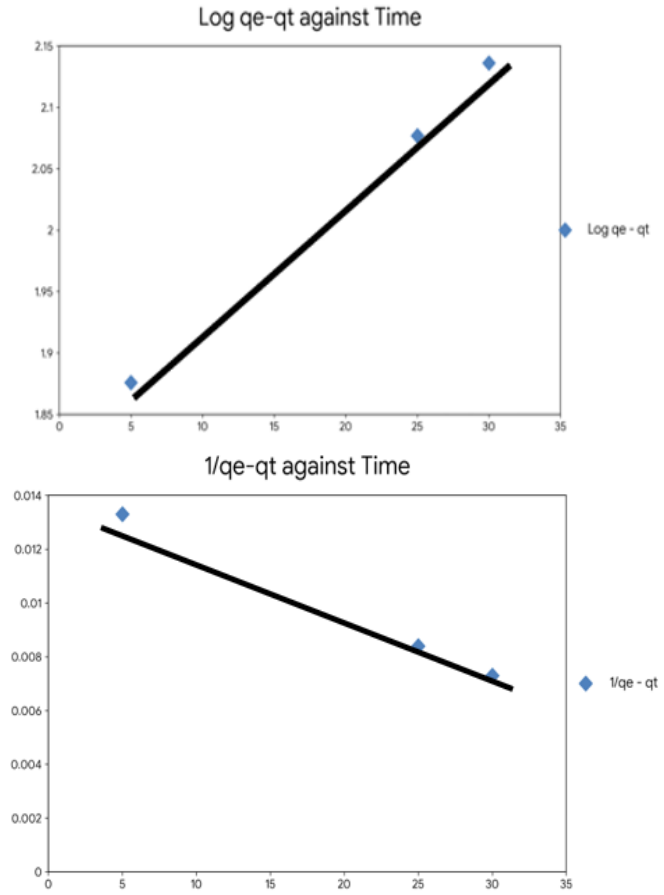


Figure 9. Showing the First Order Pseudo-Kinetics plotting Log qe-qt against time and Second Order Pseudo-Kinetics ploting 1/qe-qt against time

Conclusions

This study was conducted to evaluate the potential of groundnut husk activated carbon (GHAC) as a low-cost, sustainable, and environmentally friendly adsorbent for the removal of urea from aqueous solutions. Specifically, the research investigated the effects of adsorbent dosage, pH, contact time, and initial urea concentration on adsorption performance, while also examining the adsorption isotherms and kinetics governing the process.

The findings revealed that GHAC possesses considerable adsorption capacity for urea removal, with optimum performance achieved at an adsorbent dosage of 0.8 g, pH 0.9, and a contact time of 30 minutes. The adsorption process was strongly influenced by solution pH and adsorbent dosage, while higher initial urea concentrations enhanced adsorption efficiency. Isotherm analysis showed that the Freundlich model provided the best fit to the experimental data, indicating heterogeneous surface characteristics and multilayer

adsorption. Furthermore, kinetic studies demonstrated that the adsorption process followed a pseudo-second-order model, suggesting that chemisorption was the dominant mechanism controlling urea uptake.

The significance of these findings lies in the demonstration that agricultural waste materials such as groundnut husks can be converted into effective adsorbents for wastewater treatment. The use of GHAC offers a cost-effective and sustainable approach to mitigating nitrogen pollution, reducing environmental contamination, and supporting wastewater management in agricultural, industrial, and municipal sectors. The rapid adsorption rate and favorable adsorption characteristics further highlight its potential for practical applications in water purification systems.

Despite these promising results, the study has some limitations. The experiments were conducted under controlled laboratory conditions using synthetic urea solutions, which may not fully represent the complexity of real wastewater systems. In addition, thermodynamic studies, regeneration and reusability assessments, surface modification investigations, and column-scale experiments were not carried out. Therefore, further research is recommended to evaluate the performance of GHAC in real wastewater treatment scenarios, assess its long-term stability and regeneration potential, and optimize its application for large-scale industrial use.

Recommendations

1. Advanced Surface Modification: Chemical activation using acids, bases, or metal salts should be explored to enhance the surface area and introduce additional functional groups that may increase adsorption capacity.
2. Real Wastewater Application: Future studies should apply GHAC to real wastewater from farms, abattoirs, or fertilizer plants to assess its performance in complex matrices with competing ions.
3. Thermodynamic Studies: Investigating the thermodynamics of the adsorption process enthalpy, Gibbs free energy, and entropy would provide deeper insight into the mechanisms driving urea uptake.
4. Regeneration and Reusability: Regeneration studies using mild solvents or thermal treatment should be conducted to evaluate cost-effectiveness and long-term operational sustainability.
5. Hybrid Adsorbent Systems: Combining GHAC with other adsorbents (e.g., zeolites, clay, biochar) could create composite materials with improved performance through synergistic effects.

Author Contributions

WOM contributed to the study design. Data collection tools were designed by EAM. Initial analysis and coding were conducted by SCM who also wrote the fIrst draft of the manuscript with routine critical reviews by EI. All authors then critically reviewed the following versions. All authors have read and approved the final version of the paper and its submission and have given consent for publication.

Declaration of Generative AI and AI-Assisted Technologies in Scientific Writing

CHATgpt was used for some aspects of the research work and editing.

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Data Availability Statement

All relevant data are available within the manuscript

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None

Conflict of Interest

The authors declare that they have no conflicts of interest.

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