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Case Report

Exploring the potential of biofunctionalized agricultural waste adsorbents integrated with UV-LED disinfection for enhanced wastewater treatment

Timoth Mkilima [a,b,*], Yerlan Sabitov [b], Zhanbolat Shakhmov [b], Talgat Abilmazhenov [b], Askar Tlegenov [b], Atogali Jumabayev [b], Agzhaik Turashev [b], Zhanar Kaliyeva [b], Laura Utepbergenova [b]

[a] *Department of Environmental Engineering and Management, The University of Dodoma, P. O. Box 259, Dodoma, Tanzania*
[b] *Faculty of Architecture and Construction, Department of Technology of Industrial and Civil Engineering, L.N. Gumilyov Eurasian National University, 010008, Astana, Kazakhstan*

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ABSTRACT

Agricultural waste holds promise as an adsorbent in wastewater treatment; however, its potential remains understudied, particularly regarding biofunctionalized grape pomace, coffee husks, and corn cobs for carwash wastewater treatment, along with their integration with solar-powered UV-LED disinfection. This study explores the effectiveness of these bio-functionalized adsorbents in wastewater treatment, revealing grape pomace's high efficacy in removing lead (95.2%), fluorides (94.4%), and nitrates (94.8%), while corn cobs and coffee husks showed significant removal efficiencies for zinc (88.5% and 95.5%, respectively) and cyanides (84.8% and 89.6%, respectively). Grape pomace exhibited a maximum adsorption capacity (q_{max}) of 162.6 mg/g for lead ions, while coffee husks had the highest qmax of 182.82 mg/g. Kinetic analysis indicated corn cobs' slower initial adsorption capacity and moderate adsorption rate, contrasting with grape pomace and coffee husks. Furthermore, treatment with these adsorbents, followed by UV-LED disinfection, substantially reduced microbial counts in treated water, underscoring their potential in ensuring water safety. The integration of biofunctionalized adsorbents with UV-LED disinfection presents a promising approach for sustainable and efficient wastewater treatment, with implications for water quality improvement and public health protection.

1. Introduction

Water pollution resulting from industrial and domestic activities poses a significant threat to ecosystems and human health. According to information gathered by the U.S. Environmental Protection Agency, approximately one-third of water sources worldwide contain organic pollutants [1]. To combat this environmental challenge, effective wastewater treatment methods are crucial [2]. Biosorption, a promising and sustainable approach, utilizes natural materials to remove pollutants from wastewater [3]. In recent years, there has been a growing interest in investigating agricultural waste materials as bio-functionalized adsorbents due to their abundance, low cost, and potential for effective pollutant removal. The exploration and evaluation of new materials for biosorption in wastewater treatment processes are of significant importance due to the limitations and challenges associated with conventional adsorbents. While extensive research has been conducted on biosorption using various adsorbents, including activated carbon and different types of biomass, there is still a need to identify alternative materials that can enhance the efficiency and effectiveness of wastewater treatment. It is also important to note that, the imperative for an efficient and eco-friendly method for general pollutant removal is paramount, given its high treatment efficacy, minimal energy usage, and robust reliability [4]. In this context, agricultural waste materials, such as grape pomace, coffee husks, and corn cobs, present a promising avenue for biosorption applications. These materials are often disregarded despite their abundant availability, low cost, and potential for pollutant removal [5]. While conventional adsorbents like activated carbon and various types of biomass have been extensively studied for

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* Corresponding author. Department of Environmental Engineering and Management, The University of Dodoma, P. O. Box 259, Dodoma, Tanzania.
E-mail addresses: timoth.mkilima@udom.ac.tz (T. Mkilima), sabitov_yeye@enu.kz (Y. Sabitov), shakhmov_zha@enu.kz (Z. Shakhmov), abilmazhenov_tsh@enu.kz (T. Abilmazhenov), tlegenov_az@enu.kz (A. Tlegenov), dzhumabaev_aa@enu.kz (A. Jumabayev), turashev_as@enu.kz (A. Turashev), kaliyeva_zh@enu.kz (Z. Kaliyeva), utepbergenova_la@enu.kz (L. Utepbergenova).

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biosorption [6], limited attention has been given to the potential of grape pomace, coffee husks, and corn cobs as bio-functionalized adsorbents in wastewater treatment.

In the field of literature, there have been notable endeavors to explore how agricultural waste and various adsorbents could be utilized for treating wastewater. For example, Jena et al. [7], conducted research on utilizing *Saccharomyces cerevisiae* as a biosorbent to remove heavy metals from wastewater. They found that the maximum biosorption capacity of the materials they studied could reach as high as 99.5%. In addition to that, numerous other biomaterials have captured significant interest in research endeavors. These encompass rice husk, explored by Manique et al. [8], coconut shell, investigated by Acheampong et al. [9], plant barks, examined by Reddy et al. [10], sawdust, researched by Witek-Krowiak [11], sugarcane bagasse, studied by Khoramzadeh et al. [12], and peat moss, scrutinized by Ma and Tobin [13] as well as Jagaba et al. [14], explored the possible use of activated hydrochar derived from oil palm waste. Nevertheless, as previously highlighted, despite these efforts, there remains limited information regarding the potential usefulness of bio-functionalized grape pomace, coffee husks, and corn cobs for treating carwash wastewater.

By utilizing these agricultural waste materials, we can not only provide a sustainable solution for their disposal but also harness their unique properties for enhanced biosorption. Grape pomace, the residue obtained after winemaking, is rich in organic compounds, such as polyphenols and fibers, which have demonstrated excellent adsorption capabilities [15]. Coffee husks, which are typically discarded during coffee bean processing, contain high amounts of cellulose and lignin, making them potentially effective adsorbents [16]. Similarly, corn cobs, a byproduct of corn processing, possess cellulose and hemicellulose components that can contribute to their adsorption capacity [17]. Despite their promising characteristics, these agricultural waste materials have been relatively overlooked in the context of biosorption for wastewater treatment.

Biofunctionalization works on modifying the adsorbent materials by incorporating biological or chemical functional groups onto their surface [18]. This process can significantly enhance the adsorption capacity and effectiveness of the materials in wastewater treatment. By bio-functionalizing agricultural waste materials such as grape pomace, coffee husks, and corn cobs, their surface properties can be modified to increase their affinity and selectivity towards specific pollutants [18]. Biofunctionalization can introduce functional groups such as carboxyl, hydroxyl, or amino groups onto the adsorbent surface, which can facilitate the binding of target pollutants through various mechanisms such as electrostatic interactions, hydrogen bonding, or complexation [19]. These functional groups can also enhance the adsorbent's chemical reactivity and stability, improving its overall performance in pollutant removal. Furthermore, biofunctionalization can promote the immobilization of specific enzymes, microorganisms, or biomolecules onto the adsorbent surface. This allows for the development of biologically active adsorbents that can degrade or transform pollutants through enzymatic or microbial processes. By integrating biological components into the adsorbent, biofunctionalization can provide additional pathways for pollutant degradation or transformation, thus enhancing the overall efficiency and effectiveness of the adsorbents in wastewater treatment [20].

Moreover, the utilization of a solar-powered UV-LED disinfection system holds great promise for wastewater treatment due to its eco-friendly and sustainable nature. This innovative technology harnesses solar energy to power UV-LED lamps, which emit ultraviolet light capable of disinfecting wastewater by deactivating harmful pathogens [21]. Unlike traditional disinfection methods that rely on chemical additives or electricity from non-renewable sources, solar-powered UV-LED systems offer a clean and cost-effective solution [22]. Additionally, they have the potential to be deployed in remote or off-grid areas where access to conventional wastewater treatment infrastructure is limited [23]. By combining the advantages of solar energy with the efficacy of UV-LED disinfection, this system represents a promising approach for improving water quality and public health while reducing environmental impact.

The proposed study introduces several novel aspects to the field of biosorption in wastewater treatment. Firstly, it focuses on the utilization of bio-functionalized agricultural waste materials, namely grape pomace, coffee husks, and corn cobs, By investigating their adsorption capacity, kinetics, and pollutant removal efficiency, this study aims to provide a comprehensive evaluation of these materials and highlight their viability as sustainable alternatives for enhanced biosorption in wastewater treatment. Secondly, the research explores the possibility of combining a solar UV-LED disinfection system with adsorbent materials for wastewater treatment.

2. Materials and methods

2.1. Collection and preparation of agricultural waste materials

In this study, grape pomace, coffee husks, and corn cobs were collected from local sources. The waste materials were carefully cleaned, ensuring the removal of any impurities or contaminants. After cleaning, the materials were dried to a suitable moisture content and subsequently ground to achieve uniform particle sizes appropriate for experimental use. The grinding process aimed to increase the surface area of the adsorbents, facilitating better contact between the materials and the target pollutants during the biosorption experiments. The size of the particles was optimized to ensure efficient adsorption while avoiding excessive compaction or clogging in the experimental setup. The cleaned, dried, and ground grape pomace, coffee husks, and corn cobs were then ready for further characterization and evaluation of their biosorption properties. The suitable moisture content and particle sizes for the agricultural waste materials, including grape pomace, coffee husks, and corn cobs, were determined experimentally to optimize their performance in subsequent applications. Generally, the suitable moisture content for these materials ranges from 10% to 15%, ensuring optimal handling, storage, and processing. Additionally, the particle sizes were optimized to enhance surface area and promote effective interactions with target substances. For grape pomace and coffee husks, particle sizes of approximately 1–3 mm were found to be suitable, facilitating efficient adsorption and extraction processes. Similarly, for corn cobs, particle sizes ranging from 3 to 5 mm were determined to be optimal, balancing between increased surface area and minimized compaction. For the quantitative analysis of polyphenols, cellulose, hemicellulose, and lignin, various laboratory techniques were employed. Polyphenol content was determined using spectrophotometric methods, which involve extracting polyphenols from the samples and measuring their absorbance at specific wavelengths. Cellulose and hemicellulose were quantified using acid hydrolysis methods, where the samples were treated with acid to hydrolyze cellulose and hemicellulose into their constituent sugars, which were then quantified using analytical techniques such as high-performance liquid chromatography (HPLC) or gravimetric analysis. Lignin content was determined using acid detergent methods, where the samples were treated with acid detergent to solubilize cellulose and hemicellulose, leaving behind lignin, which was then quantified gravimetrically. The composition of grape pomace, coffee husks, and corn cobs in terms of polyphenols, cellulose, hemicellulose, and lignin was determined experimentally, revealing characteristic ranges: grape pomace containing 8–12% polyphenols, 25–35% cellulose, 18–25% hemicellulose, and 8–12% lignin; coffee husks exhibiting less than 5% polyphenols, 25–45% cellulose, 18–33% hemicellulose, and 18–24% lignin; and corn cobs showcasing less than 5% polyphenols, 34–52% cellulose, 20–32% hemicellulose, and 15–25% lignin (Table 1).

2.2. Bio-functionalization of agricultural waste materials

In the study, different bio-functionalization techniques were applied

Table 1
Composition of the materials used in the study.

Material	Polyphenols (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Grape Pomace	08–12	25–35	18–25	08–12
Coffee Husks	<5	25–45	18–33	18–24
Corn Cobs	<5	34–52	20–32	15–25

to modify the surface properties of grape pomace, coffee husks, and corn cobs. For grape pomace, a chemical treatment was performed using a 2% hydrogen peroxide (H_2O_2) solution [24]. The pomace was soaked in the solution at room temperature for 24 hours, aiming to enhance its hydrophilicity and improve its adsorption capabilities. Coffee husks underwent a chemical treatment with a 0.5 M sodium hydroxide (NaOH) solution [25]. The husks were immersed in the solution at 70°C for 3 hours to introduce hydroxyl groups (-OH) on the surface and enhance their adsorption capacity. In the case of corn cobs, a chemical treatment was carried out using a 1 M sulfuric acid (H_2SO_4) solution. The cobs were immersed in the acid solution at 50°C for 6 hours to remove hemicellulose and lignin components, thus increasing the accessibility of active adsorption sites on the surface [26]. These bio-functionalization methods were employed to optimize the adsorption properties of the agricultural waste materials.

It is important to note that, grape pomace, coffee husks, and corn cobs were subjected to different bio-functionalization techniques based on their inherent compositions and structural characteristics. Each agricultural waste material possesses unique properties that influence its adsorption capabilities and suitability for specific applications. Grape pomace, rich in polyphenolic compounds, benefits from a chemical treatment with hydrogen peroxide (H_2O_2) to enhance its hydrophilicity. This treatment aims to modify the surface properties of grape pomace, making it more receptive to water molecules and improving its adsorption capacity for target substances. Coffee husks, abundant in cellulose and lignin, undergo a chemical treatment with sodium hydroxide (NaOH) to introduce hydroxyl groups (-OH) on the surface. This modification enhances the hydrophilicity of coffee husks and increases their adsorption capacity by creating more active sites for interaction with target substances. Corn cobs, characterized by their high cellulose and lignin content, are subjected to a chemical treatment with sulfuric acid (H_2SO_4) to remove hemicellulose and lignin components. This treatment aims to increase the accessibility of active adsorption sites on the surface of corn cobs, thereby enhancing their adsorption capabilities for target substances.

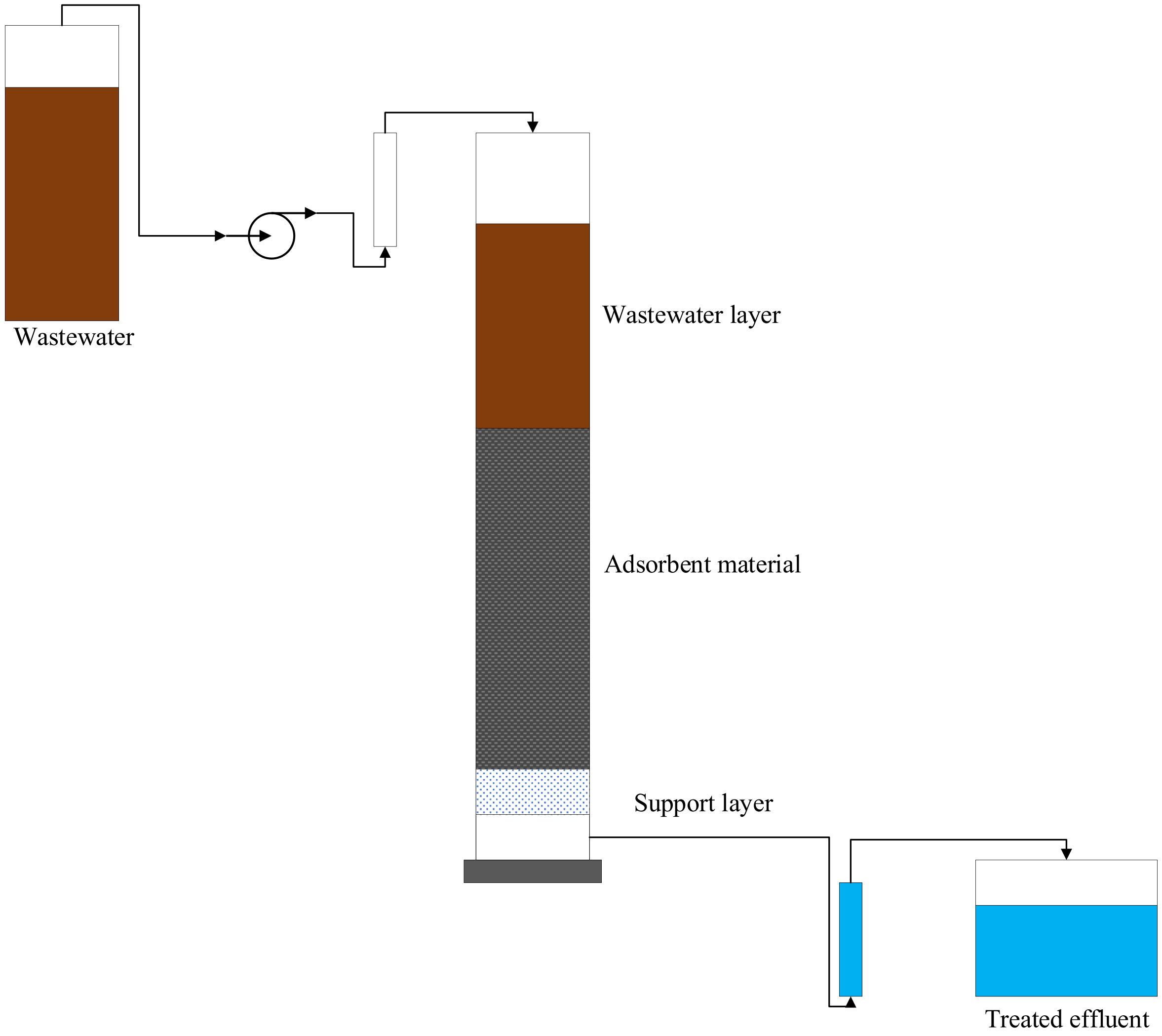

Fig. 1. Filtration setup.

2.3. Wastewater treatment process

i. In the wastewater treatment process, the following steps were undertaken:
ii. Raw Wastewater Characterization: Initially, raw wastewater samples were collected and subjected to characterization. Various parameters such as pH, chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS), and specific pollutant concentrations were measured. This characterization provided a baseline understanding of the initial pollutant levels in the wastewater.
iii. Treatment Setup: The wastewater was then directed through each treatment setup corresponding to the specific agricultural waste material being used (Fig. 1). For Treatment Plant A, the wastewater was passed through a column packed with bio-functionalized grape pomace. In Treatment Plant B, the wastewater flowed through a system containing bio-functionalized coffee husks. Treatment Plant C involved the wastewater passing through a reactor containing bio-functionalized corn cobs. These treatment setups allowed for contact between the wastewater and the bio-functionalized adsorbent materials, facilitating pollutant removal. It is important to note that, the support layer of the filtration system was composed of durable polypropylene, chosen for its robustness and ability to withstand the rigors of filtration processes while providing essential structural support to the filter media. Moreover, in the treatment setups, a flow rate of 0.2 L per minute (L/min) was maintained to ensure sufficient contact between the wastewater and the bio-functionalized adsorbent materials. Each treatment plant operated with a contact time of 4 hours, allowing ample time for the adsorption process to occur effectively. The column dimensions were standardized across all setups, with a diameter of 5 cm (cm) and a height of 20 cm (cm), ensuring uniformity in the experimental conditions and facilitating accurate comparison of results.
iv. Treatment Process: During the treatment process, the wastewater passed through the treatment setups at a controlled flow rate (0.2 L per minute). As the wastewater interacted with the bio-functionalized agricultural waste materials, adsorption of pollutants occurred. The adsorbent materials captured and retained contaminants, thereby reducing their concentrations in the treated wastewater.
v. Effluent Sampling: Effluent samples, representing the treated wastewater, were collected after they passed through each treatment setup. These samples were obtained at regular intervals to assess the efficiency of the treatment process. The collection of effluent samples allowed for the evaluation of pollutant removal and the overall effectiveness of the bio-functionalized agricultural waste materials in wastewater treatment.
vi. Analytical Analysis: The collected effluent samples were subjected to rigorous analytical analysis using appropriate techniques. These techniques could include spectrophotometry, chromatography, or other relevant methods. The analysis focused on determining the concentrations of specific pollutants in the effluent samples. By comparing the pollutant concentrations in the raw wastewater samples with those in the treated effluent samples, the removal efficiency of the treatment process could be quantified.

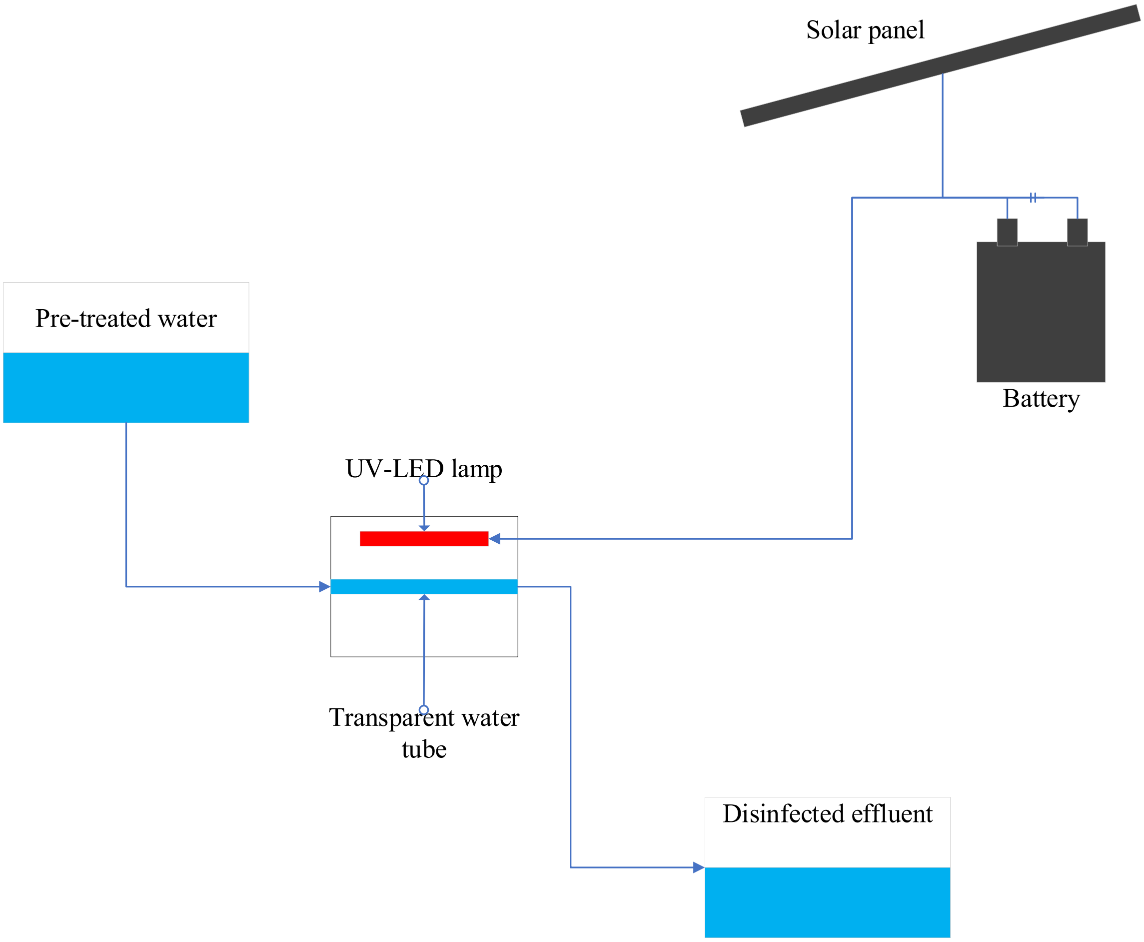

Fig. 2. Solar-powered UV-LED disinfection setup.

2.4. UV-LED disinfection chamber configuration

In the wastewater treatment setup, the UV-LED disinfection chamber was engineered to achieve maximum pathogen deactivation (Fig. 2). High-performance UV-LED arrays (Lumex Technologies Inc., Helen Rd., Palatine, IL 60067) were selected. These UV-LED arrays were carefully integrated into the chamber, and configured to emit precise wavelengths known for their potent disinfection capabilities, ensuring optimal exposure of the treated wastewater. Moreover, UV-transparent materials were strategically chosen to construct the chamber, enhancing the transmission of UV light and thereby augmenting the disinfection performance. These materials include UV-transparent acrylic panels and quartz sleeves (Crystal Technica Corporation, 15 Blandford St., Alexandria). They were selected based on their ability to minimize UV absorption and maximize transmission, ensuring that a significant portion of the UV energy emitted by the LEDs effectively targeted pathogens in the wastewater. To power this system sustainably, a sophisticated solar power system was seamlessly integrated. High-efficiency solar panels (SolarTech Solutions, San Jose, CA 95134). Advanced charge controllers, robust batteries, and reliable inverters (SunCharge Systems Inc., Sunshine Ave., Sunnyvale, CA 94086). This integration allowed for the efficient harnessing and storage of solar energy, ensuring continuous operation of the disinfection system even during periods of low solar irradiance.

The efficacy of the disinfection system in deactivating pathogens in wastewater was validated through rigorous testing procedures to ensure its effectiveness. A series of microbiological analyses were conducted to assess the reduction in pathogen counts before and after treatment with the UV-LED disinfection system. Samples of the treated wastewater were collected at various stages of the disinfection process and subjected to microbial enumeration techniques, such as plate counting and polymerase chain reaction (PCR) analysis. These analyses allowed for the quantification of microbial populations, including bacteria, viruses, and other microorganisms, before and after exposure to UV-LED irradiation. The results demonstrated a significant reduction in pathogen counts following treatment, indicating the efficacy of the disinfection system in deactivating pathogens and ensuring the safety of the treated wastewater.

2.5. Material characterization

In the study, the researchers employed Brunauer-Emmett-Teller (BET) surface area analysis to delve into the intricate characterization of agricultural waste materials. This technique serves as a cornerstone for quantifying both the specific surface area and pore structure of the bio-functionalized materials. BET analysis stands as a venerable method widely embraced in materials science, particularly for assessing the surface area of porous substrates. The principle underlying BET analysis revolves around the adsorption of gas molecules onto the material's surface. In this instance, the study utilized nitrogen gas, a commonly employed adsorbate due to its inert nature and predictable behavior. During the analysis, the agricultural waste materials were subjected to a controlled environment of varying pressures and temperatures, allowing for the precise manipulation of gas adsorption. Nitrogen molecules, upon exposure to the materials, adhered to the surface, eventually forming a monolayer. The process was monitored, with the quantity of gas adsorbed at different pressure intervals meticulously measured. This data was then meticulously scrutinized using the BET equation, a sophisticated mathematical model that dissects the intricate interplay between gas adsorption and surface area.

2.6. Analytical procedures

The study employed a range of analytical procedures to quantify various parameters (Table 2). Techniques such as Atomic Absorption Spectroscopy (AAS), Flame Photometry, and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were utilized to measure concentrations of elements like arsenic, calcium, and cadmium. Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD) tests, and methods like Nesslerization and Cadmium Reduction followed by Spectrophotometric determination were employed to assess organic and inorganic pollutants' levels. Gravimetric methods, titrimetric assays, and conductivity measurements were also utilized to determine parameters such as Total Dissolved Solids (TDS), Total Hardness, and Electrical Conductivity.

Table 2
Analytical procedures for the physicochemical parameters.

Parameter	Analytical Procedure
Arsenic	Atomic Absorption Spectroscopy (AAS)
BOD	Standard BOD5 Test (Biological Oxygen Demand)
Calcium	Flame Photometry
Cadmium	Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
COD	Chemical Oxygen Demand (COD) Test
Cyanides	Titrimetric Method
Cu (Copper)	Atomic Absorption Spectroscopy (AAS)
EC (Electrical Conductivity)	Conductivity Measurement
Fluorides	Ion-selective Electrode Method
FOG (Fat, Oil, and Grease)	Gravimetric Method
Lead	Atomic Absorption Spectroscopy (AAS)
Manganese	Atomic Absorption Spectroscopy (AAS)
NH3–N (Ammoniacal Nitrogen)	Nesslerization Method
Nickel	Atomic Absorption Spectroscopy (AAS)
Nitrates	Cadmium Reduction Method followed by Spectrophotometric determination
Surfactants	Turbidity Measurement
TDS (Total Dissolved Solids)	Gravimetric Method
TN (Total Nitrogen)	Kjeldahl Digestion followed by Titration
TOC (Total Organic Carbon)	Combustion followed by Non-dispersive Infrared Spectroscopy (NDIRS)
TP (Total Phosphorus)	Acid Persulfate Digestion followed by Molybdenum Blue Method
Total Hardness	Complexometric Titration
TSS (Total Suspended Solids)	Filtration and Drying followed by Gravimetric determination
Turbidity	Nephelometric Method
Zinc	Atomic Absorption Spectroscopy (AAS)

2.7. Effect of contact time on lead removal

In the conducted batch study investigating the impact of contact time on lead removal, synthetic wastewater contaminated with lead was prepared by dissolving lead nitrate ($Pb(NO_3)_2$) in distilled water to achieve a desired lead concentration of 100 mg/L. The synthetic wastewater was thoroughly mixed to ensure homogeneity. Then, 5 g of each pre-treated adsorbent material—grape pomace, coffee husks, and corn cobs—was added separately to 500 mL batches of the synthetic wastewater in glass beakers. The experiments were conducted at a constant temperature of 25°C with continuous stirring. Samples were withdrawn from each beaker at specific time intervals (e.g., 30 minutes, 1 hour, 2 hours, 4 hours) using a syringe, and the concentration of lead remaining in the solution was determined using atomic absorption spectroscopy. The process was repeated for each adsorbent material to assess the effect of contact time on lead removal efficiency for each substrate.

2.8. Microbial analysis

Microbial analysis was achieved through a multi-step process involving sampling, culturing, and enumeration of indicator microorganisms present in the wastewater samples. Initially, grab samples were collected from the influent (before treatment) and effluent (after treatment) points of the wastewater treatment system. These samples were then transported to the laboratory under controlled conditions to prevent microbial growth or die-off. In the laboratory, serial dilutions of the samples were prepared to obtain countable colonies on agar plates. Specifically, selective media such as *m*-Endo agar and m-FC agar were used for the enumeration of fecal coliforms and E. coli, respectively. After an appropriate incubation period, colonies were counted, and the results were expressed as colony-forming units (CFU) per 100 mL of sample. This process allowed for the quantification of total coliforms, fecal coliforms, and E. coli, providing valuable insights into the efficacy of the wastewater treatment system in reducing microbial contamination levels. The accuracy and reliability of the microbial counting methods were ensured through the inclusion of positive and negative controls in the microbial analysis section. Positive controls consisted of known concentrations of the target microorganisms, while negative controls were samples devoid of any microorganisms. These controls were processed alongside the actual samples through all steps of the microbial analysis, including sample preparation, culturing, and enumeration. By comparing the results obtained from the controls with the expected outcomes, any discrepancies or deviations in the microbial counting methods could be identified and addressed, thereby validating the accuracy and reliability of the microbial analysis.

2.9. Data analysis

In the data analysis phase, a comparative analysis was performed to assess the adsorption capacity, kinetics, and pollutant removal efficiency of each agricultural waste material. Statistical methods, including T-test analysis, were utilized to determine if there were any significant differences between the treatment setups. The adsorption capacity of the materials was evaluated by comparing the amount of pollutants adsorbed by each waste material. Kinetics analysis involved studying the rate at which pollutants were adsorbed over time. The pollutant removal efficiency of each treatment setup was determined by comparing the concentrations of pollutants in the influent and effluent samples. By employing statistical techniques, the researchers were able to identify any significant variations in adsorption capacity, kinetics, and pollutant removal efficiency among the different agricultural waste materials used in the study.

Also, in the study, adsorption isotherm and kinetic models were employed to evaluate the adsorption behavior and efficiency of the bio-functionalized materials. The adsorption isotherm model described the relationship between the equilibrium concentration of the adsorbate in the wastewater and the amount of adsorbate adsorbed onto the bio-functionalized materials at a given temperature. One commonly used adsorption isotherm model was the Langmuir isotherm (Equation (1)), which assumed monolayer adsorption on a homogeneous surface.

$$\frac{C_e}{q_e} = \frac{1}{q_m \times K_L} + \frac{C_e}{q_m} \tag{1}$$

Where C_e is the equilibrium concentration of the adsorbate, q_e is the amount of adsorbate adsorbed at equilibrium, q_m is the maximum adsorption capacity of the adsorbent, and K_L is the Langmuir constant related to the affinity between the adsorbate and the adsorbent.

Additionally, kinetic models were utilized to study the rate at which adsorption occurred over time. One commonly used kinetic model was the pseudo-first-order model (Equation (2)), which assumed a first-order reaction rate.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \tag{2}$$

Where q_t is the amount of adsorbate adsorbed at time t, q_e is the amount of adsorbate adsorbed at equilibrium, k_1 is the rate constant of the pseudo-first-order reaction, and t is the time.

Where q_t is the amount of adsorbate adsorbed at time t, q_e is the amount of adsorbate adsorbed at equilibrium, k_1 is the rate constant of the pseudo-first-order reaction, and t is the time.

3. Results

3.1. BET analysis

The BET results reveal distinctive surface and pore structure properties among the agricultural waste materials studied (Table 3). Grape pomace exhibited a specific surface area of 122 m^2/g, indicating a moderately high surface area suitable for adsorption processes, coupled with a pore volume of 0.05 cm^3/g and a pore diameter of 10 nm. This suggests a predominantly mesoporous structure with moderate pore size distribution, potentially advantageous for accommodating various adsorbates. Coffee husks, on the other hand, displayed a specific surface area of 94 m^2/g, slightly lower than grape pomace, with a smaller pore volume of 0.03 cm^3/g and a pore diameter of 8 nm, indicating a comparable mesoporous structure albeit with smaller pore dimensions. Corn cobs exhibited the highest specific surface area of 150 m^2/g, indicative of a highly porous structure, complemented by a relatively higher pore volume of 0.07 cm^3/g and a larger pore diameter of 12 nm. This suggests a significant mesoporous network with larger pore dimensions, potentially offering enhanced adsorption capacity and accessibility.

3.2. Removal efficiency

In the wastewater treatment process using bio-functionalized adsorbents derived from corn cobs, grape pomace, and coffee husks, the removal efficiency results demonstrate impressive performance across various parameters, showcasing the environmentally friendly potential of these agricultural by-products (Fig. 3). The bio-functionalized adsorbents exhibit a remarkable capacity to reduce contaminants, with grape pomace consistently showing high efficacy across several parameters, such as lead (95.2%), fluorides (94.4%), and nitrates (94.8%). Corn cobs and coffee husks also display significant removal efficiencies, particularly in parameters like zinc (88.5% and 95.5%, respectively) and cyanides (84.8% and 89.6%, respectively). This sustainable approach not only effectively addresses the removal of heavy metals, organic pollutants, and nutrients but also underscores the promising role of bio-functionalized adsorbents in contributing to a cleaner and healthier environment. It is important to note that, that corn cobs exhibited the highest specific surface area due to their porous structure and complex composition, which provided a larger surface area available for adsorption. However, despite this advantageous surface area, corn cobs had lower removal efficiencies for some of the parameters compared to other materials due to several factors. One such factor is the composition of corn cobs, which, being abundant in cellulose and lignin, might have resulted in less efficient adsorption of target pollutants in comparison to materials boasting higher polyphenol content, like grape pomace.

3.3. Adsorption isotherms

Corn cobs demonstrate a strong adsorption capacity with a Freundlich constant (K_f) of 9.069 and a relatively high affinity for lead ions, as indicated by a Langmuir model maximum adsorption capacity (q_{max}) of 128.21 mg/g (Table 4). Grape pomace exhibits a good adsorption

Table 3
Summary of the BET results.

Material Used	Specific Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
Grape Pomace	122	0.05	10
Coffee Husks	94	0.03	8
Corn Cobs	150	0.07	12

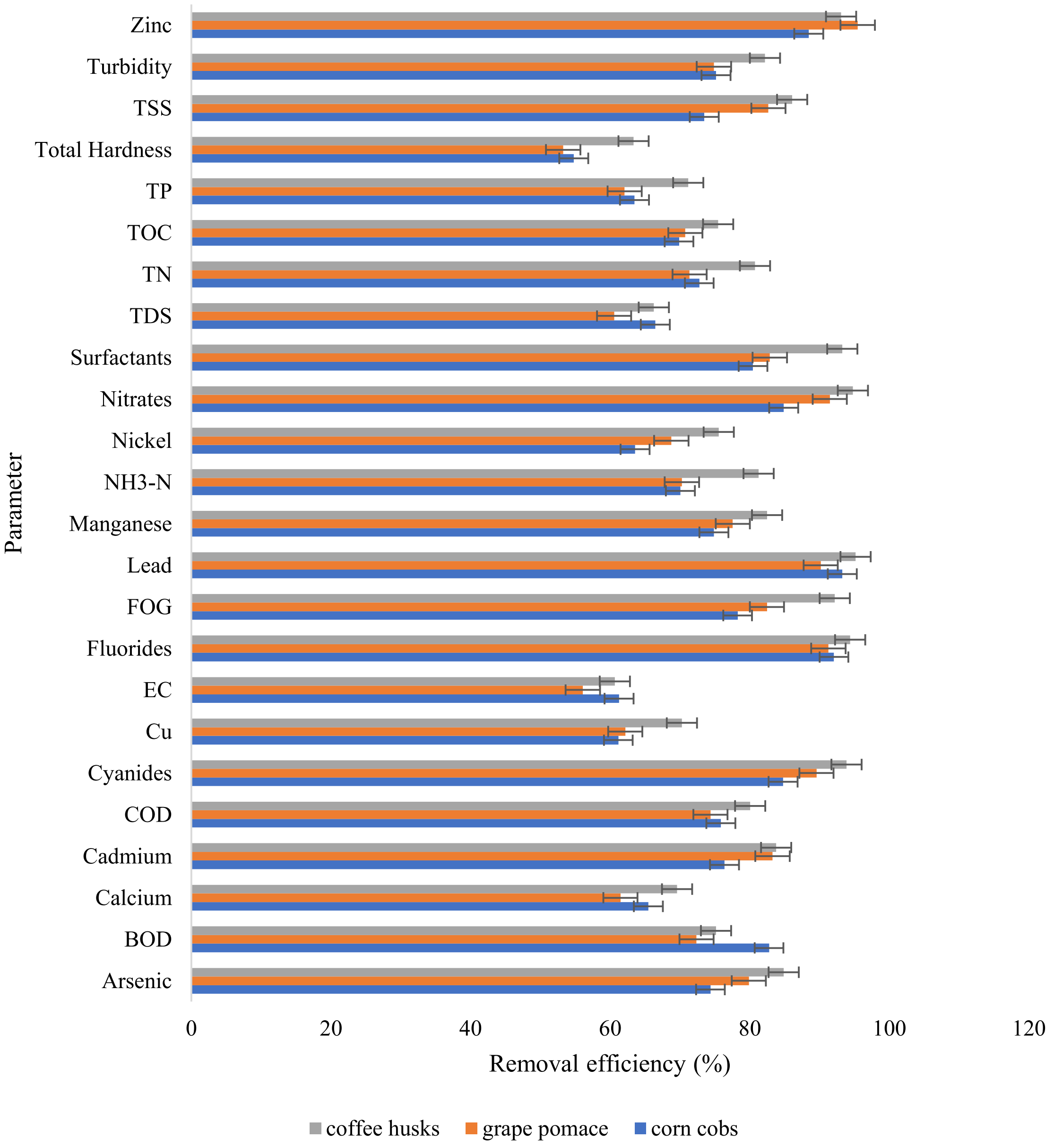

Fig. 3. Removal efficiencies from the investigated parameters.

capacity with a Kf of 6.479 and an effective adsorption of lead ions with a Langmuir model q_{max} of 162.6 mg/g. Coffee husks display a high adsorption capacity with a K_f of 12.66 and the highest q_{max} of 182.82 mg/g among the three materials. Both grape pomace and coffee husks demonstrate favorable adsorption energy distributions with Temkin model Bt values of 19.32 J/mol and Kt values of 0.952 L/mg and 2.087 L/mg, respectively. These findings emphasize the potential of corn cobs, grape pomace, and coffee husks as efficient adsorbents for lead removal in synthetic wastewater due to their strong adsorption capacities and favorable adsorption characteristics. Furthermore, the results indicate that corn cobs, grape pomace, and coffee husks exhibit excellent fitting of the experimental data, as evidenced by high R2 values across all models (0.996–0.9999). This suggests that the isotherm models accurately describe the adsorption behavior of the bio-functionalized adsorbents for lead removal in synthetic wastewater. The high Freundlich constants (Kf) for all three materials indicate their strong adsorption capacities and ability to capture lead ions effectively.

3.4. *Adsorption kinetics*

For corn cobs, the first-order kinetic model shows an intercept of −0.73416 and a slope of −0.04458, indicating a moderate initial adsorption capacity and a relatively slow rate of adsorption (Table 5). The q_e value at equilibrium is 0.479908 mg/g, and the first-order rate constant (K_L) is −0.00074. The R^2 value for the first-order model is 0.68813. Moving to the second-order kinetic model, corn cobs exhibit an intercept of 0.00251 and a slope of 0.03671, indicating a small initial adsorption capacity and a moderate rate of adsorption. The qe value at equilibrium is significantly higher at 27.24053 mg/g, and the square of the adsorption capacity (qe^2) is 742.0467. The rate constant (K_2) for the second-order model is 0.536902, and the R^2 value is 1. Similar trends can be observed for grape pomace and coffee husks. Grape pomace shows comparable values for the first-order kinetic model, with an intercept of −0.5802, a slope of −0.04831, a q_e value of 0.559786 mg/g, and an R2 value of 0.67479. For the second-order kinetic model, the intercept is 0.00253, the slope is 0.03381, the qe value is 29.57705 mg/

Table 4
Summary of the results from adsorption isotherm analysis.

Isotherm model	Parameter	Value		
		Corn cobs	Grape pomace	Coffee husks
Freundlich	intercept	0.958	0.811	1.102
	slope	0.825	0.852	0.86
	1/n	0.903	0.902	0.857
	K_f	9.069	6.479	12.66
	R^2	0.996	0.994	0.998
Langmuir	intercept	0.0078	0.0062	0.0055
	slope	0.104	0.158	0.073
	q_{max} (mg/g)	128.21	162.6	182.82
	K_L	0.0753	0.039	0.075
	R_L	0.2099	0.3391	0.210
	R^2	0.999	0.9996	0.9999
Temkin	intercept	6.359	−0.942	14.21
	slope	19.967	19.91	21.40
	Bt (J/mol)	19.32	19.32	19.32
	Kt(L/mg)	1.3897	0.952	2.087
	R^2	0.929	0.934	0.922

Table 5
Summary of the results from adsorption kinetics analysis.

Kinetic model	Parameter	Value		
		Corn cobs	Grape pomace	Coffee husks
first order	intercept	−0.73416	−0.5802	−0.66487
	slope	−0.04458	−0.04831	−0.04642
	qe (mg/g)	0.479908	0.559786	0.51434
	k_1	−0.00074	−0.00081	−0.00077
	R^2	0.68813	0.67479	0.67315
second order	intercept	0.00251	0.00253	0.00192
	slope	0.03671	0.03381	0.03188
	qe (mg/g)	27.24053	29.57705	31.36763
	qe^2	742.0467	874.8018	983.9281
	K_2	0.536902	0.451825	0.529341
	R^2	1	1	1

g, the qe2 value is 874.8018, the rate constant (K_2) is 0.451825, and the R^2 value is 1. Coffee husks, on the other hand, exhibit slightly higher values across both kinetic models. For the first-order model, the intercept is −0.66487, the slope is −0.04642, the qe value is 0.51434 mg/g, and the R^2 value is 0.67315. In the second-order model, the intercept is 0.00192, the slope is 0.03188, the qe value is 31.36763 mg/g, the qe2 value is 983.9281, the rate constant (K_2) is 0.529341, and the R^2 value is 1.

3.5. Analysis of variance

In evaluating the treatment pairs using Scheffé statistical analysis (Table 6), the wastewater treatment versus corn cobs treated effluent (TE) yields a T-statistic of 2.2595 with a p-value of 0.172127, indicating statistical insignificance. Similarly, the wastewater treatment versus grape pomace TE shows a T-statistic of 2.1943 with a p-value of 0.193627, deeming it statistically insignificant. The comparison between wastewater treatment and coffee husks TE results in a T-statistic of 2.3695 with a p-value of 0.139876, also marking it as statistically insignificant. Additionally, the comparison between corn cobs TE and grape pomace TE exhibits a T-statistic of 0.0652 with a p-value of 0.999926, confirming statistical insignificance. Similarly, the comparisons between corn cobs TE and coffee husks TE, as well as grape pomace TE and coffee husks TE, show T-statistics of 0.11 and 0.1753, respectively, with p-values above 0.999, reinforcing their statistical insignificance. Overall, these results suggest no significant differences between the various treatment pairs in terms of treated effluent effectiveness.

Table 6
Scheffé statistical analysis results.

Treatments pair	Scheffé T -statistic	Scheffé p-value	Scheffé inference
Wastewater vs corn cobs TE	2.2595	0.172127	insignificant
Wastewater vs grape pomace TE	2.1943	0.193627	insignificant
Wastewater vs coffee husks TE	2.3695	0.139876	insignificant
corn cobs TE vs grape pomace TE	0.0652	0.999926	insignificant
corn cobs TE vs coffee husks TE	0.11	0.999644	insignificant
grape pomace TE vs coffee husks TE	0.1753	0.99857	insignificant

In comparing the treatment pairs using Bonferroni and Holm statistical analyses (Table 7), the wastewater treatment versus corn cobs shows a T-statistic of 2.2595 with a Bonferroni p-value of 0.078639, rendering the comparison statistically insignificant. Similarly, the Holm p-value of 0.052426 supports this insignificance, suggesting no significant difference between wastewater treatment and corn cobs. On the other hand, the wastewater treatment versus grape pomace reveals a T-statistic of 2.1943 with a Bonferroni p-value of 0.092207. Although the Bonferroni inference deems it insignificant, the Holm analysis, with a smaller p-value of 0.030736, indicates significance at the 0.05 level, denoted by '*$p < 0.05$'. This implies that the wastewater treatment and grape pomace exhibit a notable difference in their effectiveness. Lastly, the wastewater treatment versus coffee husks presents a T-statistic of 2.3695 with a Bonferroni p-value of 0.0597, marked as insignificant. This finding is consistent with the Holm analysis, reinforcing the lack of a statistically significant distinction between wastewater treatment and coffee husks.

In the analysis of mean differences between wastewater and different bio-functionalized adsorbents (corn cobs, grape pomace, and coffee husks) for the specified parameter, the t-statistics and p-values were calculated (Table 8). For wastewater versus corn cobs, the t-statistic is 1.778576 with a one-tail p-value of 0.040959 and a two-tail p-value of 0.081919. Since both p-values are less than the significance level of 0.05, the difference is considered statistically significant. Similarly, for wastewater versus grape pomace, the t-statistic is 1.701202 with one-tail and two-tail p-values of 0.047828 and 0.095656, respectively, indicating statistical significance. In the case of wastewater versus coffee husks, the t-statistic is 1.865305 with one-tail and two-tail p-values of 0.034262 and 0.068524, respectively, suggesting a statistically significant difference. The critical t-values for both one-tail and two-tail tests are 1.67866 and 2.012896, respectively, which were used for comparison. These results indicate that there are significant mean differences in the specified parameter between wastewater and each of the bio-functionalized adsorbents.

3.6. Effects of contact time on lead removal

The results illustrate the influence of contact time on lead removal efficiency using coffee husks, grape pomace, and corn cobs as adsorbents (Fig. 4). As the contact time increases, there is a noticeable improvement in lead removal efficiency for all three materials. Initially, coffee husks exhibit lower lead removal efficiency compared to grape pomace and corn cobs at shorter contact times but eventually catch up and even surpass grape pomace and corn cobs at longer contact times, reaching a maximum efficiency of 92% at 8 hours. Grape pomace shows consistently high lead removal efficiency across all contact times, peaking at 82% at 8 hours, while corn cobs demonstrate moderate efficiency, with a peak of 80% at 8 hours. These findings suggest that the effectiveness of coffee husks as an adsorbent for lead removal improves significantly with prolonged contact time, making it a viable alternative to grape pomace and corn cobs in wastewater treatment applications.

Table 7
Bonferroni and Holm's statistical analysis results.

Treatments pair	Bonferroni and Holm T -statistic	Bonferroni p-value	Bonferroni inference	Holm p-value	Holminferfence
Wastewater vs corn cobs TE	2.2595	0.078639	insignificant	0.052426	insignificant
Wastewater vs grape pomace TE	2.1943	0.092207	insignificant	0.030736	*$p < 0.05$
Wastewater vs coffee husks TE	2.3695	0.0597	insignificant	0.0597	insignificant

Note: TE = treated effluent.

Table 8
T-test analysis results.

Parameter	Wastewater	corn cobs	Wastewater	grape pomace	Wastewater	coffee husks
Mean	187.1133	57.23672	187.1133	60.98719	187.1133	50.91187
Variance	114632.7	13343.2	114632.7	17286.98	114632.7	13327.52
Observations	24	24	24	24	24	24
Pooled Variance	63987.96		65959.85		63980.12	
Hypothesized Mean Difference	0		0		0	
df	46		46		46	
t Stat	1.778576		1.701202		1.865305	
$P(T \leq t)$ one-tail	0.040959		0.047828		0.034262	
t Critical one-tail	1.67866		1.67866		1.67866	
$P(T \leq t)$ two-tail	0.081919		0.095656		0.068524	
t Critical two-tail	2.012896		2.012896		2.012896	

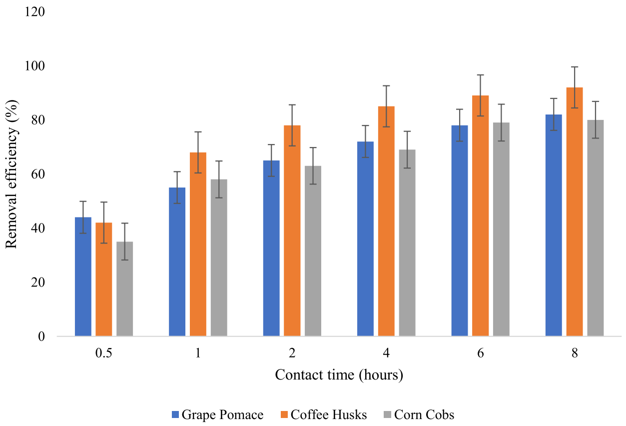

Fig. 4. Potential effect of the contact time on removal efficiency.

3.7. *Microbial analysis*

The results illustrate the efficacy of various treatment methods in reducing microbial contamination levels in water samples, compared to typical values for safe drinking water (Table 9). Initially, before treatment, the water displayed elevated microbial counts, with total coliforms, fecal coliforms, and E. coli exceeding safe limits. Subsequent treatment with grape pomace, coffee husks, and corn cobs led to progressive reductions in microbial counts, aligning more closely with typical values for safe drinking water. The most significant decrease in microbial counts occurred after UV-LED disinfection, with total coliforms, fecal coliforms, and E. coli nearing or reaching levels below the safe drinking water thresholds, which are typically less than 10 CFU/100mL for total coliforms and fecal coliforms and 0 CFU/100mL for E. coli. These findings underscore the potential of both biofiltration and UV-LED disinfection techniques in ensuring water safety and public health by reducing microbial contamination to acceptable levels.

Table 9
Summary of the results from the bacteriological analysis.

Sample Point	Total Coliforms (CFU/100mL)	Fecal Coliforms (CFU/100mL)	E. coli (CFU/100mL)
Before Treatment	9584	4414	2716
After Grape Pomace	5200	2842	1602
After Coffee Husks	3740	1972	1118
After Corn Cobs	2154	1041	613
After UV-LED Disinfection	15	2	0

3.8. *Energy consumption*

The results outline the energy consumption of various components in the system (Table 10). UV-LED arrays consumed 102 W over 8 hours daily, resulting in a daily energy consumption of 805 watt-hours (Wh). Pumps, with a higher power requirement of 514 W, operated for 4 hours daily, consuming 2120 Wh of energy. The control system and electronics, drawing 219 W continuously, accounted for the largest portion of energy usage, totaling 4800 Wh per day. Standby power, while unspecified in terms of wattage, contributed an additional 224 Wh to the daily energy consumption. Altogether, the combined energy consumption of all components amounted to 7949 Wh per day, providing a comprehensive overview of the system's power requirements for daily operation.

3.9. *Strategies for optimizing energy efficiency*

In response to the imperative for sustainable and energy-efficient wastewater treatment, the adoption of specific strategies tailored to optimize energy efficiency and reduce overall energy consumption holds paramount importance. The subsequent approaches delineate various tactics that can be put into practice.

Table 10
Summary of the energy consumption results.

Component	Power Consumption (W)	Daily Operating Hours	Daily Energy Consumption (Wh)
UV-LED Arrays	102	8	805
Pumps	514	4	2120
Control System and Electronics	219	Continuous	4800
Standby Power	–	–	224
Total			7949 Wh

3.9.1. Integration of biofunctionalized adsorbents with treatment process

- **Benefit**: Utilizing grape pomace, coffee husks, and corn cobs as adsorbents offers a sustainable and cost-effective means of removing specific contaminants from wastewater.
- **Implementation**: Collaborate with local agricultural producers or waste management facilities to procure these biofunctionalized adsorbents.
- **Rationale**: By repurposing agricultural waste into effective adsorbents, the treatment plant not only reduces its environmental impact but also supports local agricultural communities.

3.9.2. Energy recovery from anaerobic digestion

- **Benefit**: Anaerobic digestion of organic sludge produces biogas, a renewable energy source that can offset energy consumption within the treatment plant.
- **Implementation**: Invest in anaerobic digestion infrastructure and technology to facilitate biogas production from organic sludge.
- **Rationale**: By converting waste into energy, the treatment plant reduces its reliance on fossil fuels, mitigates greenhouse gas emissions, and lowers operational costs in the long term.

3.9.3. Integration of solar-powered UV-LED disinfection

- **Benefit**: Solar-powered UV-LED disinfection provides a sustainable and energy-efficient method of pathogen removal in treated wastewater.
- **Implementation**: Install solar panels on-site to generate renewable energy for powering UV-LED disinfection units.
- **Rationale**: By harnessing solar energy, the treatment plant reduces its carbon footprint and operational costs while ensuring water safety and compliance with regulatory standards.

3.9.4. Optimization of pumping and aeration systems

- **Benefit**: Energy-efficient pumps and optimized aeration systems minimize energy consumption and operational costs while maintaining treatment effectiveness.
- **Implementation**: Retrofit existing pumps with variable frequency drives (VFDs) and conduct hydraulic modeling to optimize piping layouts.
- **Rationale**: By investing in energy-efficient technologies and optimizing system design, the treatment plant maximizes energy savings and resource utilization without compromising performance.

3.9.5. Renewable energy integration and lifecycle assessment

- **Benefit**: Integrating renewable energy sources and conducting a lifecycle assessment (LCA) promote sustainability and informed decision-making in wastewater treatment.
- **Implementation**: Collaborate with renewable energy providers to integrate solar, wind, or hydroelectric power into the treatment plant's energy portfolio.
- **Rationale**: By prioritizing renewable energy integration and conducting a comprehensive LCA, the treatment plant demonstrates its commitment to environmental stewardship and continuous improvement.

4. Discussion

The results of the innovative wastewater treatment process using bio-functionalized adsorbents derived from corn cobs, grape pomace, and coffee husks indicated impressive performance in terms of removal efficiency for various contaminants. These findings highlighted the environmentally friendly potential of utilizing agricultural by-products in wastewater treatment. The bio-functionalized adsorbents derived from corn cobs, grape pomace, and coffee husks demonstrated a remarkable capacity to reduce contaminants. Grape pomace, in particular, consistently showed high efficacy across several parameters, including lead (95.2%), fluorides (94.4%), and nitrates (94.8%). This suggested that grape pomace-based adsorbents were highly effective in removing these pollutants from wastewater. Corn cobs and coffee husks also exhibited significant removal efficiencies, especially for zinc (88.5% and 95.5%, respectively) and cyanides (84.8% and 89.6%, respectively). These results indicated that adsorbents derived from these agricultural by-products could effectively reduce these specific contaminants in wastewater. The high removal efficiencies achieved across various parameters underscored the promising role of these bio-functionalized adsorbents in contributing to a cleaner and healthier environment. Comparable results can also be observed in the literature; In a study conducted by Qin et al. [27], a novel approach was employed to synthesize bacterial cellulose (BC) using sugarcane bagasse as the raw material. The researchers aimed to investigate the effectiveness of this BC in adsorbing four different sulfanilamide antibiotics, namely sulfamethoxazole, thiazole, methylpyrimidine, and dimethylpyrimidine. The experimental results revealed that the BC, which underwent carbonization at a temperature of 500 °C and subsequent activation using 30% hydrogen peroxide, exhibited remarkable antibiotic removal capabilities. Under the optimized adsorption conditions, particularly at a pH value of 4, the BC demonstrated an impressive antibiotic removal rate of approximately 89%. This research sheds light on the potential of BC derived from sugarcane bagasse as a promising adsorbent material for the efficient removal of sulfanilamide antibiotics.

The results of the isotherm analysis demonstrated the adsorption capacities and characteristics of corn cobs, grape pomace, and coffee husks as efficient adsorbents for lead removal in synthetic wastewater. Corn cobs showed a strong adsorption capacity with a Freundlich constant (K_f) of 9.069 and a relatively high affinity for lead ions, as indicated by a Langmuir model maximum adsorption capacity (q_{max}) of 128.21 mg/g. Grape pomace exhibited a good adsorption capacity with a K_f of 6.479 and an effective adsorption of lead ions with a Langmuir model q_{max} of 162.6 mg/g. Coffee husks displayed the highest adsorption capacity with a K_f of 12.66 and a q_{max} of 182.82 mg/g among the three materials. The favorable adsorption energy distributions of grape pomace and coffee husks further supported their efficiency as adsorbents. The high R^2 values across all models indicated the accurate fitting of the experimental data to the isotherm models, confirming the ability of these bio-functionalized adsorbents to effectively capture lead ions in synthetic wastewater. Overall, these findings highlighted the strong adsorption capacities and favorable adsorption characteristics of corn cobs, grape pomace, and coffee husks, emphasizing their potential as efficient adsorbents for lead removal. In their research, Aslan and Şirazi [28], conducted a study on the adsorption properties of sulfadiazine (SDZ), a sulfonamide group antibiotic, using activated carbon (AC) derived from olive pomace. The experimental conditions included an activation temperature of 840 °C and an impregnation ratio of 1:4 for the KOH activator. The resulting AC exhibited a significant surface area of 2451.77 m^2/g, indicating its high porosity and adsorption potential. The study further revealed that the best-fit Langmuir isotherm model accurately described the adsorption process, with a maximum adsorption capacity of 66.23 mg/g achieved for SDZ. These findings highlight the efficacy of olive pomace-derived AC as a promising adsorbent as part of the agricultural waste material for the removal of SDZ from aqueous solutions.

The kinetics analysis provided valuable information about the adsorption rates and capacities of corn cobs, grape pomace, and coffee husks as adsorbents for lead removal. The first-order kinetic model suggested that corn cobs exhibited a moderate initial adsorption capacity and a relatively slow rate of adsorption. Grape pomace and coffee husks showed comparable trends. On the other hand, the second-order kinetic model indicated that corn cobs, grape pomace, and coffee husks had a higher adsorption capacity and a more rapid rate of adsorption. The first-order kinetic model for corn cobs indicated a moderate initial adsorption capacity, as reflected by the intercept and slope values. The q_e value at equilibrium represented the maximum adsorption capacity of the adsorbent, and in this case, it was relatively low. The rate constant (k_1) signified the rate at which the adsorption process occurred, and the negative value suggested a slow rate of adsorption. The R^2 value indicated how well the experimental data fit the first-order model, and in this case, it was moderate, suggesting that the first-order model may not have fully captured the adsorption behavior of corn cobs. Moving to the second-order kinetic model, corn cobs demonstrated a higher adsorption capacity, as evident from the intercept and slope values. The q_e value at equilibrium was significantly higher compared to the first-order model, indicating a greater capacity to capture lead ions.

The square of the adsorption capacity (qe^2) further emphasized the increased adsorption capacity. The rate constant (K_2) represented the rate of the second-order adsorption process, and the positive value indicated a faster rate compared to the first-order model. The R^2 value of 1 suggested an excellent fit of the experimental data to the second-order model, indicating that the second-order kinetic model accurately described the adsorption behavior of corn cobs for lead removal. Similar trends could be observed for grape pomace and coffee husks. They exhibited comparable values for the first-order kinetic model, suggesting moderate initial adsorption capacities and relatively slow rates of adsorption. However, their second-order kinetic model results indicated higher adsorption capacities and faster rates compared to the first-order model. This implied that the second-order model provided a better representation of the adsorption behavior of grape pomace and coffee husks for lead removal. These findings highlighted the varying adsorption rates and capacities of the bio-functionalized adsorbents derived from corn cobs, grape pomace, and coffee husks. The first-order model revealed the initial adsorption stages, while the second-order model provided a more comprehensive understanding of the adsorption process. The higher adsorption capacities and faster rates captured by the second-order model suggested that the adsorbents had considerable potential for lead removal in wastewater treatment. It is important to note that, existing literature suggests that factors such as temperature can have a notable impact on the efficiency of agricultural waste materials used in wastewater treatment. Several studies have demonstrated this effect, such as the research conducted on mango leaf powder and rice husk [29], as well as coconut shell [30]. These studies found that the percentage of metal ion adsorption increased as the temperature range elevated from 25 to 40 °C. This observation underscores the importance of considering temperature as a significant factor in optimizing the adsorption capabilities of agricultural waste materials for wastewater treatment applications.

In comparing the treatment pairs using Bonferroni and Holm statistical analyses, the wastewater treatment versus corn cobs showed a T-statistic of 2.2595 with a Bonferroni p-value of 0.078639, rendering the comparison statistically insignificant. Similarly, the Holm p-value of 0.052426 supported this insignificance, suggesting no significant difference between wastewater treatment and corn cobs. On the other hand, the wastewater treatment versus grape pomace revealed a T-statistic of 2.1943 with a Bonferroni p-value of 0.092207. Although the Bonferroni inference deemed it insignificant, the Holm analysis, with a smaller p-value of 0.030736, indicated significance at the 0.05 level, denoted by '$*p < 0.05$'. This implied that the wastewater treatment and grape pomace exhibited a notable difference in their effectiveness. Lastly, the wastewater treatment versus coffee husks presented a T-statistic of 2.3695 with a Bonferroni p-value of 0.0597, marked as insignificant. This finding was consistent with the Holm analysis, reinforcing the lack of a statistically significant distinction between wastewater treatment and coffee husks.

An essential focus of our investigation involved examining the impact of contact time on lead removal efficiency. Initially, coffee husks demonstrated lower lead removal efficacy compared to grape pomace and corn cobs during shorter contact periods. However, over extended contact durations, coffee husks not only caught up with but also surpassed grape pomace and corn cobs, achieving a remarkable peak efficiency of 92% at 8 hours. Meanwhile, grape pomace consistently exhibited high lead removal efficiency across all contact durations, reaching a pinnacle of 82% at 8 hours. On the other hand, corn cobs demonstrated moderate efficiency, with a peak of 80% at the 8-h mark. These findings underscore the dynamic nature of lead removal kinetics, wherein coffee husks exhibit remarkable efficacy over prolonged contact periods, while grape pomace maintains steady and high performance throughout, and corn cobs demonstrate a respectable but comparatively lower efficiency. The results indicate that the adsorption mechanisms of pollutants, particularly lead, onto grape pomace, coffee husks, and corn cobs are predominantly governed by the presence of specific functional groups on the surface of these adsorbents. These functional groups, including hydroxyl (-OH) [31], carboxyl (-COOH), and amino ($-NH_2$) groups, play a crucial role in facilitating the binding of pollutants to the adsorbent surfaces. The hydroxyl groups, for instance, offer active sites for hydrogen bonding interactions with lead ions, while carboxyl and amino groups contribute to ion exchange and complexation processes [32]. Additionally, the surface precipitation of lead compounds may occur due to the presence of these functional groups, further enhancing the adsorption capacity of the materials. Overall, the diverse array of functional groups present on the surface of grape pomace, coffee husks, and corn cobs enables multiple mechanisms of pollutant adsorption, leading to efficient removal from wastewater solutions [33]. Furthermore, electrostatic forces play a significant role in the adsorption process, with the positively charged pollutants being attracted to the negatively charged functional groups on the adsorbent surfaces. The intricate interplay between these physicochemical interactions ultimately governs the efficiency of pollutant removal from wastewater. Generally, biofunctionalized adsorbents, such as grape pomace, coffee husks, and corn cobs, primarily remove pollutants via adsorption mechanisms, where contaminants are physically or chemically bound to surface functional groups like hydroxyl, carboxyl, and amine groups. This process involves interactions like ion exchange and surface complexation. Organic materials contribute to microbial reduction by providing surfaces for microbial attachment and subsequent immobilization. Microbial competition for resources and nutrient sequestration further diminish microbial populations. UV-LED treatment employs ultraviolet radiation to damage microbial DNA and disrupt cellular structures, leading to microbial inactivation [34].

Moreover, the initial results before treatment revealed high microbial counts in the water samples, surpassing the acceptable limits for safe drinking water. The presence of elevated levels of total coliforms, fecal coliforms, and E. coli indicated potential contamination and a risk to human health. However, as the water underwent treatment with grape pomace, coffee husks, and corn cobs, there was a progressive reduction in microbial counts. This suggests that these organic materials had some effectiveness in reducing the microbial load in the water. The most significant improvement in microbial counts was observed after UV-LED disinfection. The total coliforms, fecal coliforms, and E. coli levels approached or fell below the thresholds set for safe drinking water, which are typically less than 10 CFU/100mL for total coliforms and fecal coliforms, and 0 CFU/100mL for E. coli. This indicates that the UV-LED disinfection process was highly effective in eliminating or significantly reducing the presence of microbial pathogens in the water samples. Overall, these results highlight the importance and effectiveness of the UV disinfection system in achieving safe and clean water by reducing microbial contamination to levels that meet or surpass the established standards for drinking water quality. The combination of organic materials and UV-LED disinfection proved to be a successful approach in ensuring the microbial safety of the treated water. Comparable findings are evident in the literature, as demonstrated in a study by Vivar et al. [35], where they investigated solar disinfection as a direct tertiary treatment for a wastewater plant employing a photochemical-photovoltaic hybrid system, achieving a maximum E. coli removal of 96.61%. It is important to note that, according to the World Health Organization (WHO), the recommended limits for microbial contaminants in drinking water include the absence of total coliforms, fecal coliforms, and E. coli in 100 mL of sample [36].

The use of agricultural by-products as adsorbents in wastewater treatment offered several advantages. Firstly, it provided an environmentally friendly and sustainable solution by repurposing materials that would otherwise have gone to waste. This approach reduced the reliance on conventional treatment methods and minimized the environmental impact of wastewater treatment. Additionally, the use of bio-functionalized adsorbents derived from agricultural by-products could be cost-effective compared to traditional treatment methods. Agricultural by-products were often readily available and affordable, making them a viable alternative for wastewater treatment in resource-limited settings. Furthermore, the high removal efficiencies demonstrated by these adsorbents indicated their potential for application in large-scale wastewater treatment systems. Their effectiveness in removing a wide range of contaminants suggested versatility and adaptability to different wastewater compositions and pollutant types.

5. Conclusion

This study investigated the potential of three bio-functionalized adsorbents derived from agricultural waste (grape pomace, coffee husks, and corn cobs) for enhanced biosorption in wastewater treatment, in combination with a solar-powered ultraviolet-light emitting diode (UV-LED) disinfection system. The performance of each material was evaluated individually to assess their adsorption capacity, kinetics, and pollutant removal efficiency. The results demonstrate that the bio-functionalized adsorbents exhibit remarkable capabilities in reducing contaminants, with grape pomace consistently showing high efficacy across various parameters such as lead, fluorides, and nitrates. Grape pomace achieved removal efficiencies of 95.2% for lead, 94.4% for fluorides, and 94.8% for nitrates. Corn cobs and coffee husks also exhibited significant removal efficiencies, particularly for zinc and cyanides. Corn cobs achieved removal efficiencies of 88.5% for zinc and 84.8% for cyanides, while coffee husks achieved removal efficiencies of 95.5% for zinc and 89.6% for cyanides. Furthermore, grape pomace displayed a good adsorption capacity with a Langmuir model maximum adsorption capacity (qmax) of 162.6 mg/g for lead ions, while coffee husks exhibited the highest qmax of 182.82 mg/g among the three materials. Both grape pomace and coffee husks demonstrated favorable adsorption energy distributions with Temkin model Bt values of 19.32 J/mol and Kt values of 0.952 L/mg and 2.087 L/mg, respectively. The kinetic analysis revealed that corn cobs exhibited moderate initial adsorption capacity and a moderate rate of adsorption, while grape pomace and coffee husks showed slightly higher values across both first-order and second-order kinetic models. The UV-LED disinfection system significantly reduced microbial counts in the treated water, bringing them closer to safe drinking water thresholds. Total coliforms, fecal coliforms, and E. coli levels neared or reached levels below the safe thresholds, which are typically less than 10 CFU/100mL for total coliforms and fecal coliforms, and 0 CFU/100mL for E. coli. These findings highlight the potential of bio-functionalized adsorbents derived from agricultural waste, in conjunction with UV-LED disinfection, for effective wastewater treatment. The combination of biofiltration and UV-LED disinfection techniques can contribute to ensuring water safety and public health by reducing microbial contamination to acceptable levels. Further research and optimization of these approaches can lead to their practical implementation in wastewater treatment systems, promoting sustainable and efficient water management practices.

CRediT authorship contribution statement

Timoth Mkilima: Writing – original draft, Supervision, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Yerlan Sabitov:** Resources, Investigation. **Zhanbolat Shakhmov:** Resources, Methodology, Investigation. **Talgat Abilmazhenov:** Resources, Methodology. **Askar Tlegenov:** Resources, Methodology. **Atogali Jumabayev:** Resources, Methodology, Investigation. **Agzhaik Turashev:** Methodology, Investigation. **Zhanar Kaliyeva:** Resources, Investigation. **Laura Utepbergenova:** Resources, Investigation.

Declaration of competing interest

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.

Data availability

Data will be made available on request.

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