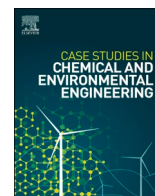




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## Case Report

## Investigating the potential of wheat straw and pistachio shell as a bio-functionalized agricultural waste biomass for enhanced biosorption of pollutants from wastewater



Timoth Mkilima<sup>a,\*</sup>, Yerkebulan Zharkenov<sup>b</sup>, Aisulu Abduova<sup>c</sup>, Nursulu Sarypbekova<sup>c</sup>, Kamilya Kirgizbayeva<sup>d</sup>, Iliyas Zhumadilov<sup>e</sup>, Farida Kenzhekulova<sup>f</sup>, Mukhtarov Abilkhas<sup>g</sup>, Shyngys Zharassov<sup>h</sup>

<sup>a</sup> Department of Environmental Engineering and Management, The University of Dodoma, P. O. Box 259, Dodoma, Tanzania

<sup>b</sup> Department of Civil Engineering, L.N. Gumilyov Eurasian National University, Kazakhstan

<sup>c</sup> Department of Ecology, M. Auezov South Kazakhstan Research University, Kazakhstan

<sup>d</sup> Department of Standardization, Certification and Metrology, L.N. Gumilyov Eurasian National University, Kazakhstan

<sup>e</sup> Department of Geodesy and Civil Engineering, Shakarim University, Semey City, Kazakhstan

<sup>f</sup> M.H. Dulati Taraz Regional University, Kazakhstan

<sup>g</sup> Department of Biotechnology and Microbiology, L.N. Gumilyov Eurasian National University, Kazakhstan

<sup>h</sup> Research Laboratory of Applied Mechanics and Robotics, Karaganda Buketov University, Kazakhstan

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## ABSTRACT

The management of wastewater from carwash centers continues to pose a significant global challenge, with the quest for treatment methods that are both effective and economical proving particularly daunting. This underscores the importance of exploring natural materials for wastewater treatment. However, knowledge regarding the efficacy of bio-functionalized wheat straw and pistachio shells specifically for carwash wastewater treatment remains limited. This study explored the potential of wastewater treatment using bio-functionalized agricultural waste materials, specifically wheat straw and pistachio shells. Experimental setups included treatment plants using wheat straw alone, pistachio shell alone, a mixture of both, and a series connection. Removal efficiencies across various water quality parameters revealed the series connection as the most effective treatment, achieving exceptional removal efficiencies for critical parameters such as fat, oil, and grease, total suspended solids, and turbidity. The Mixture treatment demonstrated synergistic effects, surpassing individual treatments in removing contaminants such as Arsenic, Biochemical Oxygen Demand, cadmium, Chemical Oxygen Demand, fluorides, ammonia nitrogen, and surfactants. More precisely, the series treatment setup resulted in nearly complete removal efficiency, approximately 100%, for Fat, Oil, and Grease, turbidity, and total suspended solids in the wastewater samples. The treatment setup using only wheat straw achieved removal efficiencies between 41.3% and 83.3%, whereas the setup using only pistachio shell achieved removal efficiencies ranging from 43.3% to 89.1%. Statistical analyses confirmed the significance of observed differences, with isotherm and kinetic models providing valuable insights into adsorption characteristics. Freundlich constants ranged from 3.6 to 12.38. Moreover, the integrated treatments consistently outperformed individual ones, as demonstrated by Water Quality Index values. The Water Quality Index values ranged from 2114.26 for raw wastewater, classified as “unsuitable for drinking,” to 154.47 for the series connection of wheat straw and pistachio shell, indicating a significant improvement in water quality.

## 1. Introduction

Agriculture, as a cornerstone industry essential for meeting the

world's sustenance needs, exhibits a paradoxical facet by contributing substantially to environmental challenges through the annual production of immense quantities of waste. This paradox underscores the

\* Corresponding author.

E-mail address: [tmkilima@gmail.com](mailto:tmkilima@gmail.com) (T. Mkilima).

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pressing need for a paradigm shift in the industry's waste management practices, which has burgeoned into a formidable challenge, exacerbated by the relentless growth of the global population [1]. The intricate interplay between the expansion of agricultural activities and the simultaneous increase in population accentuates the complexity of this issue [2,3]. The burgeoning global population not only places an increased demand on agricultural production but also contributes to the daily generation of substantial volumes of wastewater originating from diverse sources around the world [4]. Yevich and Logan [5] highlight the substantial annual generation of agricultural waste, reaching billions of tons in both developing and developed nations. This waste encompasses various materials such as leaves, straw, husks, hulls, shells, and animal dung, left behind in fields after harvest or removed during crop processing at mills. Despite the diverse range of agricultural residue, only a select few types serve as significant biomass fuels. Additionally, livestock production produces vast amounts of manure, with global estimates of around 13 billion tons generated each year [8]. These figures highlight the magnitude of agricultural waste generation and the need for effective waste management strategies. Looking ahead, future trends indicate that the quantity of waste generated through agriculture is likely to increase as global food demand continues to rise. The Food and Agriculture Organization of the United Nations (FAO) predicts that global food production needs to increase by 70% to meet the needs of a projected population of 9.7 billion by 2050 [6]. This increase in food production will inevitably lead to a proportional increase in agricultural waste generation and, consequently, an intensified need for efficient waste management and wastewater treatment solutions. This dual challenge, characterized by the coexistence of copious agricultural waste and escalating wastewater production, underscores the critical nature of wastewater treatment on a global scale [7]. The exponential growth in population exacerbates the urgency of addressing this issue as the demand for food and other agricultural products intensifies, placing unprecedented stress on natural resources. As we navigate this intricate landscape, the inefficacy of current wastewater treatment and management techniques compounds the challenges at hand [8]. Despite significant advancements in various fields, including technology and environmental science, finding effective and sustainable solutions for treating the escalating volumes of wastewater remains elusive [9]. The persistent gap in our ability to address the dynamic nature of wastewater treatment underscores the need for innovative approaches that align with the evolving demands of a changing world. In this complex nexus of agricultural waste, population growth, and wastewater challenges, the urgency to develop comprehensive and sustainable solutions becomes paramount. The global community must not only acknowledge the existing challenges but also actively collaborate to devise strategies that balance the imperative of agricultural productivity with the preservation of our environment [10].

Amidst these challenges, an opportunity arises to address agricultural waste and wastewater treatment. Traditionally seen as a burden on the agricultural industry, waste from farming practices can become a valuable resource, serving as an adsorbent material for wastewater purification [11]. Bio-functionalization, a process enhancing the adsorption capacity of these residues, adds potential [12]. This approach not only tackles waste disposal but also positions these materials in sustainable solutions for the global water crisis. Wheat straw and pistachio shells are agricultural byproducts often overlooked after the main crop harvest. Wheat straw is the stalk left over after wheat grains are harvested [13], and pistachio shells are the outer layers discarded during the processing of pistachio nuts [14]. Both materials, usually considered as waste, have unique properties that make them suitable for bio-functionalization and application in wastewater treatment. Their abundant availability, low cost, and natural characteristics contribute to their potential as effective adsorbents in removing pollutants from wastewater when subjected to bio-functionalization processes [15]. This repurposing of agricultural residues demonstrates a sustainable and environmentally friendly approach to addressing both waste

management and water purification challenges [16]. Bio-functionalization is a process that involves modifying agricultural residues at a molecular or biological level to enhance their functional properties [17]. In the context of wastewater treatment, this approach aims to improve the adsorption capacity of agricultural waste materials, such as wheat straw and pistachio shells. By introducing specific biological or chemical functionalities, the surface properties of these residues can be tailored to better attract and retain pollutants present in wastewater. Bio-functionalization transforms agricultural byproducts into materials with enhanced capabilities for removing contaminants, making them more effective in the purification process. This strategy contributes to the development of sustainable solutions for wastewater treatment [18]. Significant endeavors have been undertaken in utilizing waste materials for wastewater treatment. For instance, Coelho et al. [19], employed cashew nut shells to remove metal ions Cd (II), Pb (II), and Cr (III) from water. AbdurRahman et al. [20], utilized orange peels for dye removal from textile wastewater. Kamsonlian et al. [21], investigated the effectiveness of banana and orange peels for similar purposes. Additionally, Ebrahimi et al. [22], focused on eliminating arsenic contamination from water using chemically modified wheat straw. Božić et al. [23] conducted research on the removal of lead ions from aqueous solutions using beech sawdust and wheat straw through biosorption. Rambabu et al. [24] investigated the efficiency of date palm empty fruit bunch wastes for removing toxic hexavalent chromium through biosorption. Jalali et al. [25] studied the biosorption of lead ions from aqueous environments utilizing wheat stem biomass. Weng et al. [26], employed a combination of pressure steam and a base (NaOH) to process black tea powder for the purpose of removing Cu(II) ions. They achieved a maximum adsorption capacity of 43.18 mg/g at pH 4.4, with nearly 90% of Cu removal achieved after a contact period of 10 minutes. However, despite these efforts, there remains a dearth of information regarding the potential utilization of bio-functionalized wheat straw and pistachio shell for treating carwash wastewater specifically. It should be noted that carwash wastewater is termed as one of the highly polluted wastewater in the world, characterized by high levels of fats, oils, grease (FOG), total suspended solids (TSS), surfactants, and heavy metals such as lead (Pb) and cadmium (Cd).

Positioned at the forefront of an innovative trajectory, this study delves into the untapped potential of bio-functionalized agricultural waste. The focus is directed toward two agricultural byproducts often overlooked in their conventional roles—wheat straw and pistachio shell. These seemingly unassuming remnants from the agricultural process are poised to play a pivotal role in revolutionizing wastewater treatment methodologies. Exploring the transformative capabilities of wheat straw and pistachio shell through bio-functionalization aims to unlock their inherent capacities for enhanced adsorption, contributing significantly to the arsenal of sustainable tools available for combating challenges posed by contaminated water sources. The heart of the investigation lies in unraveling the intricacies of how these agricultural residues, once bio-functionalized, can serve not only as effective adsorbents but also as catalysts for ushering in a new era of environmentally conscious wastewater treatment. Undertaking a comprehensive analysis of bio-functionalized wheat straw and pistachio shell, the study seeks to pave the way for a paradigm shift in the approach to wastewater treatment. Subsequent sections will shed light on the experimental methodologies employed, the results obtained, and the potential implications of harnessing bio-functionalized agricultural waste for wastewater purification on a global scale. The experimental design of our investigation encompasses four distinct categories, each shedding light on different aspects of wastewater treatment. These categories include treatment plants utilizing wheat straw alone, pistachio shell alone, a combination of wheat straw and pistachio shell, and a series connection where the effluent from the wheat straw setup feeds into the pistachio shell treatment plant. By exploring these configurations, we aim to unravel the intricate dynamics and synergies between wheat straw and pistachio shell in wastewater purification processes, offering valuable insights

into sustainable and efficient solutions for global water challenges. To be more specific, the study delves into one such innovative avenue – the utilization of agricultural waste as a bio-functionalized adsorbent for wastewater treatment – shedding light on its potential to contribute to a more sustainable and harmonious coexistence between agricultural practices and environmental preservation.

## 2. Materials and methods

### 2.1. Experimental setup

The cylindrical containers utilized in the experimental setup were fabricated from Polyvinyl chloride (PVC) material. These containers were filled with bio-functionalized waste biomass derived from wheat straw and pistachio shell. The biomass, prepared through a bio-functionalization process, comprised a mixture of wheat straw and pistachio shell materials. To ensure uniform flow distribution within the columns, perforated plates with evenly spaced apertures covered the top surfaces of each column. A 100 L storage drum served as the source for feeding the columns, delivering wastewater at a controlled rate of 0.0035 L/s. Continuous stirring was employed to keep all solids suspended in the wastewater. The Wet-packing method was employed to fill the porous medium, minimizing layering and air entrapment within the packing. Each column was mounted vertically, with glass wool positioned at the base to provide support for the adsorbent bed. Prior to introducing the wastewater feed, the columns were flushed with deionized water, followed by the commencement of the experimental run. Filtrate samples were systematically collected at regular intervals throughout the duration of the experiments. All experimental procedures were conducted under ambient conditions, maintaining a room temperature range of 20–25 °C. Each experiment was conducted with three replicates to ensure the reliability and robustness of the results (Fig. 1).

#### 2.1.1. Biomass Selection and Pre-treatment

**Biomass Selection and Pre-treatment for Synergistic Valorization:** The study strategically combined wheat straw (*Triticum aestivum*) and pistachio shells to advance synergistic valorization. Wheat straw, known for its rich lignocellulosic content, and the unique choice of pistachio shells were integrated to explore their combined potential in waste biomass utilization, emphasizing sustainability and resource efficiency. The agricultural waste biomass, wheat straw, underwent a comprehensive process to ensure optimal substrate quality. The harvesting process involved careful collection at an appropriate growth stage, followed by cleaning to remove extraneous impurities such as soil and foreign matter. Subsequently, the collected wheat straw from a local organic farm underwent controlled oven drying to eliminate excess moisture, ensuring stable and consistent material characteristics. Simultaneously, pistachio (*Pistacia vera*) shells acquired from a local nut processing facility, selected for their pioneering role in waste biomass utilization, underwent a specialized pre-treatment. This involved soaking the shells in a sodium hydroxide solution, carefully designed to break down complex biomolecular structures and enhance the accessibility of bioactive components. Following this, a meticulous drying phase was implemented, optimizing conditions to achieve the desired physicochemical properties conducive to synergistic co-utilization with wheat straw. In tandem with wheat straw processing, a rotary blade shredder was employed to size-reduce the straw into uniform particles with an average length of 2–3 cm. This mechanical refinement aimed to enhance the surface area and accessibility of the lignocellulosic matrix for subsequent processes.

#### 2.1.2. Microbial bio-functionalization

In this critical phase, a precisely tailored microbial consortium was cultured for the explicit purpose of bio-functionalizing the wheat straw. The consortium, composed of hydrocarbon-degrading bacteria (*Pseudomonas* sp.), metal-accumulating bacteria (*Bacillus* sp.), and cellulose-

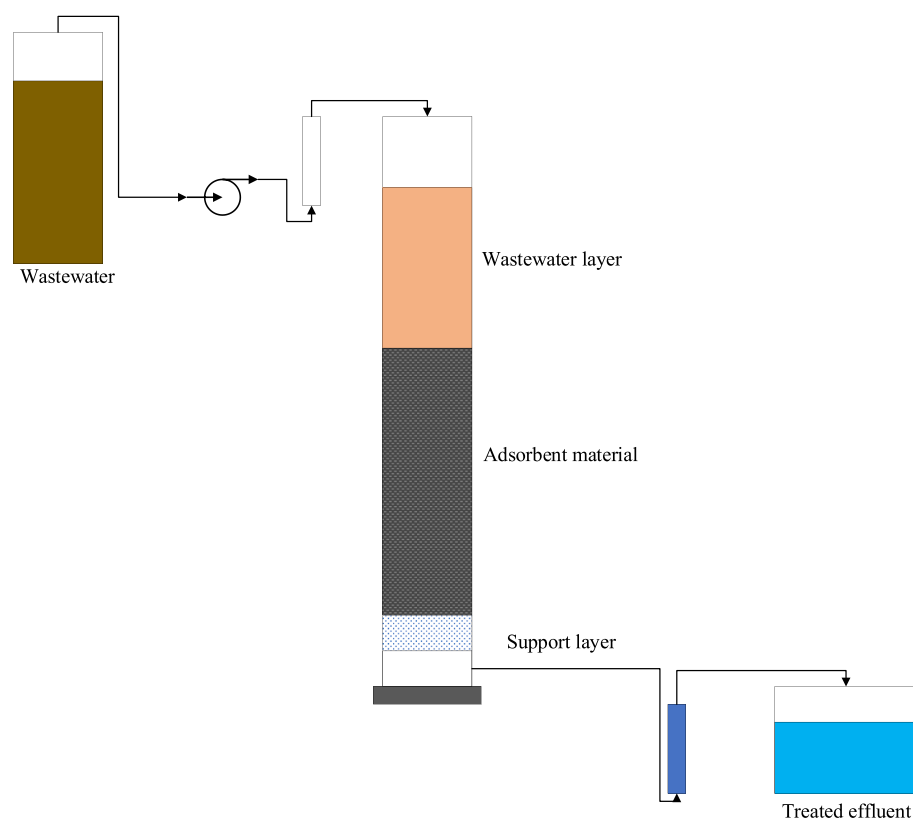


Fig. 1. General experimental setup.

decomposing fungi (*Trichoderma reesei*), underwent cultivation in a nutrient-rich liquid medium. Specifically, a 5% glucose solution supplemented with 0.1% peptone and 0.05% yeast extract was prepared using high-quality reagents (Sigma-Aldrich, St. Louis, MO, USA). During the cultivation process, which spanned 10 days at 30 °C with continuous agitation, the nutrient-rich medium served to promote the optimal growth and metabolic activities of the microbial consortium. Following this, the resulting microbial biomass underwent a meticulous harvesting process, involving centrifugation at 5000 rpm for 15 minutes using a centrifuge (Thermo Fisher Scientific, Waltham, MA, USA) to concentrate the cells. Subsequently, the harvested microbial biomass underwent a rigorous washing step using a sterile phosphate-buffered saline (PBS) solution (VWR International, Radnor, PA, USA) to effectively remove residual medium components and impurities. This washing process was repeated thrice to ensure the purity of the microbial biomass. The resulting bio-functionalized microbial consortium was then ready for its application in enhancing the characteristics of the wheat straw for subsequent processes in this innovative study.

### 2.1.3. Biomass enrichment (microbial consortium introduction and colonization)

The thoroughly washed microbial consortium, consisting of hydrocarbon-degrading bacteria (*Pseudomonas* sp.), metal-accumulating bacteria (*Bacillus* sp.), and cellulose-decomposing fungi (*Trichoderma reesei*), was precisely introduced to the prepared wheat straw particles. This introduction involved combining the microbial consortium with the wheat straw particles in a sterile environment. The colonization process was meticulously controlled by incubating the mixture at a specific temperature of 30 °C for precisely 72 hours under aerobic conditions. During this incubation period, a controlled aerobic environment was maintained to optimize microbial activity and colonization of the wheat straw biomass. Following the colonization phase, the microbial-enriched biomass underwent a carefully monitored air-drying process at room temperature. This drying phase aimed to stabilize the bio-functionalized wheat straw particles while preserving the microbial enhancements imparted during the colonization period. The resulting product was then ready for further analysis and utilization in the context of this sophisticated study.

### 2.1.4. Batch adsorption experiments (preparation of carwash wastewater and biomass interactions)

In this investigation, a batch treatment was also undertaken using wastewater contaminated with lead, with the objective of examining the kinetics and isotherms of the adsorbents. In this comprehensive study encompassing four distinct experimental categories, involving wheat straw waste biomass alone, pistachio shell alone, and a combination of the two, a precisely formulated wastewater containing lead (Pb) ions with different concentrations was prepared. The pollutant source utilized was lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ), (Sigma-Aldrich, St. Louis, MO, USA), chosen for its accuracy and reproducibility. For the first experimental category involving wheat straw waste biomass alone, 10 g of the microbial-enriched wheat straw biomass, obtained from local agricultural farms, was precisely measured and added to 100 mL of the wastewater. The same procedure was followed for the second category involving pistachio shells alone, sourced from local suppliers. In the third category, where a combination of wheat straw waste biomass and pistachio shell was utilized, a composite mixture was created by adding 5 g of microbial-enriched wheat straw biomass and 5 g of pistachio shell, both obtained from local sources to 100 mL of the wastewater. These interactions were carried out in separate batches to maintain experimental integrity and facilitate robust data analysis. To ensure the reliability of the results, all experiments were conducted in triplicate,

introducing a meticulous level of replicability across each category. This comprehensive approach aimed to account for potential variations and strengthen the statistical significance of the observed effects in the subsequent analysis of lead (Pb) ion removal by the respective biomasses in the carwash wastewater.

## 2.2. Synthetic lead-contaminated wastewater

To create synthetic wastewater containing lead for the investigation of a bio-functionalized agricultural waste biomass's performance in enhanced biosorption, a solution was prepared using deionized water as the base. Lead nitrate (Sigma-Aldrich, St. Louis, MO, USA) was added in predetermined concentrations, ranging from 10 to 100 mg/L, to simulate diverse levels of lead contamination. The pH of the synthetic wastewater was adjusted to mimic conditions typically found in polluted water sources. Subsequently, an agricultural waste biomass, derived from spent coffee grounds, was bio-functionalized through a surface modification process to enhance its affinity for lead ions. The bio-functionalized biomass was then introduced into the synthetic wastewater at controlled lead concentrations, and the biosorption process was monitored over a specified period. This methodological precision allowed for a detailed examination of the agricultural waste biomass's biosorption efficiency under varying lead concentrations, providing valuable insights into its potential as a sustainable and effective solution for pollutant remediation in water treatment applications.

## 2.3. Adsorption kinetics

This study investigates the potential of bio-functionalized agricultural waste from wheat straw and pistachio shells for wastewater treatment, focusing on adsorption kinetics. The experimental setups include four categories: (1) treatment with wheat straw alone, (2) treatment with pistachio shell alone, (3) treatment with a mixture of wheat straw and pistachio shell, and (4) a series connection where the effluent from the wheat straw setup is fed to the pistachio shell treatment plant. The adsorption capacity at equilibrium ( $q_e$ ) is a key parameter in kinetic studies, determined using Equation (1).

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

Here,  $C_0$  is the initial concentration of the adsorbate,  $C_e$  is the concentration at equilibrium,  $V$  is the volume of the solution, and  $m$  is the mass of the adsorbent.

The pseudo-first-order and pseudo-second-order kinetic models can be applied to understand the adsorption kinetics. The pseudo-first-order model is expressed using Equation (2).

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

Equation (3) represents the mathematical formulation of the pseudo-second-order model, which was utilized in this study to describe the kinetics of the system.

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} \quad (3)$$

Here,  $k_1$  and  $k_2$  are the rate constants for the respective models. These equations, along with experimental data, will be employed to assess the efficiency and synergistic effects of the bio-functionalized agricultural waste in wastewater treatment, offering a comprehensive understanding of the adsorption kinetics in the studied systems.

## 2.4. Adsorption isotherms

Adsorption isotherms describe the relationship between the amount of adsorbate (contaminant) adsorbed onto a solid surface (adsorbent) and the concentration of the adsorbate in the surrounding solution at equilibrium. Langmuir and Freundlich adsorption isotherms are two commonly used models to analyze and understand adsorption processes.

### Langmuir Adsorption Isotherm:

The Langmuir adsorption model (Equation (4)) served as the theoretical framework in our study, as it is based on the premise of monolayer adsorption, proposing that adsorption occurs exclusively at specific sites on the adsorbent surface. Furthermore, this model implies that once a site is occupied by an adsorbate molecule, no additional adsorption can occur at that particular site. Consequently, Langmuir's theory suggests the existence of a saturation point for adsorption, where further uptake of adsorbate molecules ceases, resulting in the formation of a monolayer. By applying this concept, we gained valuable insights into the dynamics of adsorption processes, thereby enhancing our understanding of adsorbent-adsorbate interactions at the molecular level.

$$q = \frac{Q_{\max} \times K_L \times C}{1 + K_L \times C} \quad (4)$$

whereby,  $q$  is the amount of adsorbate adsorbed per unit mass of adsorbent,  $C$  is the equilibrium concentration of the adsorbate in the solution,  $Q_{\max}$  is the maximum adsorption capacity, and  $K_L$  is the Langmuir adsorption constant.

### Freundlich Adsorption Isotherm:

The Freundlich adsorption model (Equation (5)) was employed in our study, providing a versatile framework for understanding multilayer adsorption phenomena on heterogeneous surfaces. Unlike the Langmuir model, Freundlich's approach accommodates variations in adsorption energy with surface coverage, making it particularly suitable for complex adsorption scenarios. This model acknowledges the heterogeneous nature of adsorbent surfaces and accounts for the possibility of multiple layers of adsorbate forming. By incorporating these factors, the Freundlich model offers a broader perspective on adsorption processes, enriching our comprehension of the intricate interactions between adsorbent and adsorbate in our experimental context.

$$q = K_F \times C^{\frac{1}{n}} \quad (5)$$

whereby,  $q$  is the amount of adsorbate adsorbed per unit mass of adsorbent,  $C$  is the equilibrium concentration of the adsorbate in the solution,  $K_F$  is the Freundlich adsorption constant,  $1/n$  is an empirical parameter related to adsorption intensity.

## 2.5. Analytical techniques

Parameter	Analytical Method	Measurement Unit
Arsenic	ICP-OES	µg/L
Biochemical Oxygen Demand (BOD)	Standard Methods 5220	mg/L
Calcium	Titration (Complexometric titration)	mg/L
Cadmium	ICP-OES	µg/L
Chemical Oxygen Demand (COD)	Standard Methods 5220D	mg/L
Cyanides	Colorimetric Method	µg/L
Copper (Cu)	ICP-OES	mg/L
Electrical Conductivity (EC)	Conductivity Meter	µS/cm
Fluorides	Ion-Selective Electrode	mg/L
Fat, Oil, and Grease (FOG)	Gravimetric Analysis	mg/L
Lead	ICP-OES	µg/L
Manganese	ICP-OES	µg/L
Ammoniacal Nitrogen (NH <sub>3</sub> -N)	Colorimetric Method	mg/L

(continued on next column)

(continued)

Parameter	Analytical Method	Measurement Unit
Nickel	ICP-OES	µg/L
Nitrates	Ion Chromatography	mg/L
Surfactants	Methylene Blue Active Substances Method	mg/L
Total Dissolved Solids (TDS)	Gravimetric Evaporation	ppm or mg/L
TN (Total Nitrogen)	Kjeldahl Digestion and Colorimetric Method	mg/L
Total Organic Carbons (TOC)	UV-Persulfate Oxidation	mg/L or ppm
Total Phosphorus (TP)	Ion Chromatography	mg/L
Total Hardness	Titration (Complexometric titration)	mg/L
Total Suspended Solids (TSS)	Standard Method 2540D	mg/L
Turbidity	Nephelometric Method (ISO 7027)	NTU
Zinc	ICP-OES	µg/L

## 2.6. Material characterization

BET (Brunauer-Emmett-Teller) analysis was employed to evaluate the surface area, pore volume, and pore size distribution of the bio-functionalized wheat straw and pistachio shell biomass. Nitrogen adsorption-desorption isotherms were measured at  $-196$  °C using a Micromeritics ASAP 2020 gas adsorption analyzer (Micromeritics Instrument Corporation, Norcross, GA 30093, USA). The isotherm data were then analyzed with Micromeritics MicroActive (6.0) software, which offers precise calculations and graphical representations of adsorption isotherms. The total pore volume was computed from the nitrogen adsorption at a relative pressure of approximately 0.99 using the Barrett-Joyner-Halenda (BJH) model, which is integrated into MicroActive. Pore size distribution analysis was also conducted with MicroActive software, enabling the characterization of micropores, mesopores, and macropores. This comprehensive analysis provided precise insights into the porous structure and adsorption properties of the bio-functionalized biomasses, essential for understanding their potential applications across various fields.

## 2.7. Data analysis

### 2.7.1. Removal efficiency

The removal efficiency when the effluent from one treatment system is fed into another system depends on various factors, including the characteristics of the pollutants, the effectiveness of each treatment system, and the nature of the combined processes. In general, if the first treatment system has already removed a significant portion of the pollutants, the effluent entering the second system would ideally have lower pollutant concentrations. The second treatment system can then target the remaining pollutants or further reduce their concentrations.

The overall removal efficiency of the combined treatment process can be calculated based on the performance of each individual system. Suppose the first system achieves a removal efficiency of  $RE_{ws}$  (expressed as a percentage) for a specific pollutant, and the second system achieves a removal efficiency of  $RE_{ps}$  for the same pollutant. The overall removal efficiency ( $RE_{overall}$ ) can be estimated using the formula:

$$RE_{overall} = 1 - \left(1 - \frac{RE_{ws}}{100}\right) \times \left(1 - \frac{RE_{ps}}{100}\right)$$

### 2.7.2. Analysis of variance

In this study, statistical analyses were conducted to assess the significance of data variations among different experimental groups. The Tukey Honestly Significant Difference (HSD) test, coupled with

Bonferroni and Holm corrections for multiple comparisons, played a crucial role in ensuring the robustness and reliability of the findings. These statistical methods were employed to discern significant differences between pairs of groups while effectively controlling the overall Type I error rate. The rigorous application of these tests enhances the credibility of the results, providing a comprehensive understanding of the data variations and contributing to the accuracy of the conclusions drawn from the study.

## 2.8. Water quality analysis based on indices

The development of Water Quality Indices (WQIs) involved combining a diverse set of 24 individual water quality parameters. The utilization of the WQI methodology enabled the consolidation of these 24 parameters into a unified composite index, efficiently simplifying the evaluation of the overall effectiveness of treatment methods, including both synthetic and natural zeolite approaches. The systematic process for formulating the WQIs is explained through Equations (1)–(4).

### 2.8.1. Parameter weight assignment

The initial step involved assigning weights ( $w_i$ ) to each parameter on a scale of 0–10, inspired by the Water Quality Index (WQI) established by the National Sanitation Foundation [27]. The relative weight ( $R_w$ ) for each parameter was calculated using Equation (1), providing a nuanced perspective on their contribution to the overall water quality [28,29].

$$R_w = \frac{w_i}{\sum_{i=1}^n w_i} \quad (1)$$

' $n$ ' symbolizes the number of parameters, ' $R_w$ ' represents the designated relative weight, and ' $w_i$ ' indicates the weight assigned to each parameter.

Table 1 furnishes a summary of the parameter weights and their corresponding relative weights computed in the study. These weights play a crucial role in the comprehensive WQIs, influencing the overall assessment of treatment methodologies encompassing both synthetic and natural zeolite approaches. The table serves as a valuable reference point for understanding the significance and contribution of individual

**Table 1**  
Weights and proportional weights assigned to the analyzed factors.

Parameter	Weight	Relative Weight
Lead	9	0.075
Arsenic	10	0.083
Cadmium	8	0.067
Cyanides	8	0.067
Fluorides	7	0.058
Nitrates	7	0.058
COD	7	0.058
TP	4	0.033
Turbidity	3	0.025
Zinc	3	0.025
Nickel	3	0.025
Manganese	4	0.033
TN	4	0.033
TOC	5	0.042
Surfactants	5	0.042
NH3-N	5	0.042
Cu	6	0.05
FOG	6	0.05
BOD	6	0.05
TDS	2	0.017
Total hardness	2	0.017
Calcium	2	0.017
TSS	2	0.017
EC	2	0.017

The units are mg/L except for color, which is measured in Pt-scale, and turbidity, which is measured in NTU.

parameters to the overall water quality evaluation.

### 2.8.2. Quality rating scale calculation

Departing from traditional methods, the quality rating scale ( $q_i$ ) for each parameter is calculated by dividing its concentration by the globally accepted guideline value and then multiplying it by 100 [28,29].

$$R_s = \frac{C_i}{S_i} \times 100 \quad (2)$$

' $R_s$ ' denotes the quality rating, ' $C_i$ ' represents the concentration of each parameter, and ' $S_i$ ' is the reference standard.

### 2.8.3. Sub-index determination

In a departure from conventional methodologies, the sub-index ( $SL_i$ ) for each parameter was determined by multiplying its relative weight ( $W_i$ ) with its quality rating ( $q_i$ ). This step, outlined in Equation (3), adds a layer of sophistication to the assessment, emphasizing the significance of each parameter in contributing to the overall water quality.

In order to derive the comprehensive WQI, the determination of the  $SL_i$  for each specific parameter was a requisite step, as outlined explicitly in Equation (3) [28,29].

$$SL_i = W_i \times q_i \quad (3)$$

### 2.8.4. Comprehensive WQI

The comprehensive WQI was constructed by summing the sub-indices derived from the assessment of each parameter [28,29].

$$WQI = \sum_{i=1}^n SL_i \quad (4)$$

### 2.8.5. Classification of water quality

Classifications based on WQI values provide a systematic way to assess the overall quality of water, categorizing it into different levels [30,31].

- Excellent water: WQI <50.
- Good quality: WQI ranging from 50 to 100.
- Poor quality: WQI ranging from 100 to 200.
- Very poor quality: WQI ranging from 200 to 300.
- Unsuitable for drinking: WQI >300

## 3. Results

### 3.1. Brunauer-Emmett-Teller data characterization

Table 2 provides the BET data for bio-functionalized wheat straw and pistachio shell biomass. The surface area of the wheat straw biomass ranges from 50 to 100 m<sup>2</sup>/g, while that of the pistachio shell biomass ranges from 50 to 150 m<sup>2</sup>/g. Similarly, the pore volume for wheat straw biomass falls between 0.1 and 0.3 cm<sup>3</sup>/g, whereas for pistachio shell biomass, it ranges from 0.05 to 0.2 cm<sup>3</sup>/g. In terms of pore size

**Table 2**  
BET data for bio-functionalized biomass.

Parameter	Value	
	Wheat Straw Biomass	Pistachio Shell Biomass
Surface Area (m <sup>2</sup> /g)	50–100	50–150
Pore Volume (cm <sup>3</sup> /g)	0.1–0.3	0.05–0.2
Pore Size Distribution		
- Micropores (<2 nm) (%)	30–40	20–30
- Mesopores (2–50 nm) (%)	50–60	60–70
- Macropores (>50 nm) (%)	5–10	5–15
Total Pore Volume (cm <sup>3</sup> /g)	0.1–0.3	0.05–0.2
Average Pore Diameter (nm)	10–20	15–25
Porosity (%)	40–50	35–45

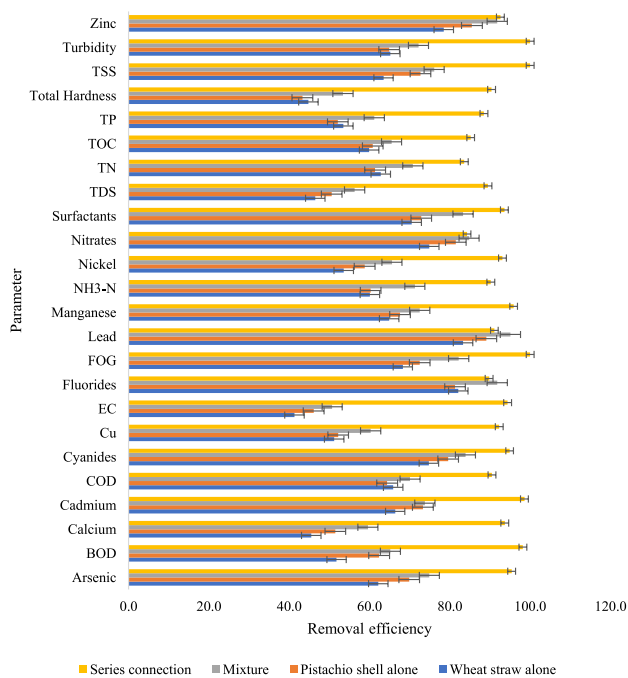


Fig. 2. Summary of the removal efficiencies.

Table 3  
Summary of the Tukey HSD results.

Treatments pair	Tukey HSD Q statistic	Tukey HSD p-value	Tukey HSD inference
A vs B	2.3033	0.482811	insignificant
A vs C	2.485	0.405096	insignificant
A vs D	2.7423	0.302913	insignificant
A vs E	4.1866	0.030055	*p < 0.05
B vs C	0.1817	0.899995	insignificant
B vs D	0.439	0.899995	insignificant
B vs E	1.8833	0.65083	insignificant
C vs D	0.2573	0.899995	insignificant
C vs E	1.7016	0.723075	insignificant
D vs E	1.4443	0.825392	insignificant

Note: A = Raw wastewater, B = treated effluent using wheat straw, C = treated effluent using pistachio shell, D = treated effluent using a mix of wheat straw and pistachio shell, E = treated effluent using a series connection of wheat straw and pistachio shell.

distribution, both biomasses exhibit varying proportions of micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). The total pore volume mirrors the individual pore volume ranges for both biomasses. Additionally, the average pore diameter ranges from 10 to 20

Table 4  
Summary of the Bonferroni and Holm results.

Treatments pair	Bonferroni and Holm T -statistic	Bonferroni p-value	Bonferroni inference	Holm p-value	Holm inference
A vs B	1.6287	1.061145	insignificant	0.742802	insignificant
A vs C	1.7572	0.815499	insignificant	0.652399	insignificant
A vs D	1.9391	0.549353	insignificant	0.494418	insignificant
A vs E	2.9604	0.037324	*p < 0.05	0.037324	*p < 0.05
B vs C	0.1285	8.979949	insignificant	0.897995	insignificant
B vs D	0.3104	7.567905	insignificant	2.270371	insignificant
B vs E	1.3317	1.855913	insignificant	1.113548	insignificant
C vs D	0.182	8.559354	insignificant	1.711871	insignificant
C vs E	1.2032	2.313605	insignificant	1.156803	insignificant
D vs E	1.0213	3.092721	insignificant	1.237088	insignificant

Note: A = Raw wastewater, B = treated effluent using wheat straw, C = treated effluent using pistachio shell, D = treated effluent using a mix of wheat straw and pistachio shell, E = treated effluent using a series connection of wheat straw and pistachio shell.

nm for wheat straw biomass and 15–25 nm for pistachio shell biomass. The porosity of the wheat straw biomass ranges from 40% to 50%, whereas that of the pistachio shell biomass ranges from 35% to 45%. These data offer insights into the structural characteristics of the bio-functionalized biomasses, which are vital for understanding their potential applications in various fields, such as adsorption, catalysis, and environmental remediation.

### 3.2. Removal efficiency

The removal efficiencies for different water quality parameters using various treatment methods (wheat straw alone, pistachio shell alone, mixture, series connection) demonstrate the effectiveness of each approach. For most parameters, the Series connection shows the highest removal efficiencies, with substantial improvements over individual treatments. Notably, Series connection achieves exceptionally high removal efficiencies for parameters like FOG, TSS, and turbidity, reaching 100% (Fig. 2). The Mixture treatment also generally outperforms individual treatments, showcasing synergistic effects. Arsenic, BOD, Cadmium, COD, Fluorides, NH<sub>3</sub>-N, and surfactants exhibit notably higher removal efficiencies across all treatments, highlighting the efficacy of the applied methods. Calcium, Cyanides, EC, Manganese, Nickel, Nitrates, TDS, TN, TOC, TP, and Total Hardness also demonstrate improved removal with the Series connection.

The Tukey HSD test was employed to evaluate the significance of differences between various treatments (Table 3). Comparing the treatments, it is evident that there are no statistically significant differences in the water quality parameters between pairs of raw wastewater and treated effluent using wheat straw resulting in a p-value of 0.483. Also, the raw wastewater and the treated effluent using pistachio shell resulted in a p-value of 0.405, raw wastewater and treated effluent using a mix of wheat straw and pistachio shell resulted in a p-value of 0.303, and the effluent treated by wheat straw and treated effluent using a series connection of wheat straw and pistachio shell resulted in a p-value of 0.651, all indicating a statically non-significant difference. However, the pair of raw wastewater vs and treated effluent using a series connection of wheat straw and pistachio shell shows a significant difference with a Tukey HSD Q statistic of 4.1866 and a p-value of 0.030055, indicating that the treated effluent using a series connection of wheat straw and pistachio shell has a significantly different water quality compared to the raw wastewater.

The statistical analysis using Bonferroni and Holm corrections for multiple comparisons was performed to assess the significance of differences between various treatments (Table 4). Comparing the treatments, it is observed that there are no significant differences in the water quality parameters between the investigated pairs. However, the pair between the raw wastewater (A) vs the treated effluent using the series connection (E) shows significant differences with a T-statistic of 2.9604 and a p-value of 0.037324, indicating that the treated effluent using a series connection of wheat straw and pistachio shell has a significantly

different water quality compared to the raw wastewater. However, it should also be noted that the observed p-values are still relatively low indicating that there were notable differences in the water quality values.

### 3.3. Adsorption isotherm

The results of the isotherm models for wheat straw, pistachio shell, and their combination reveal valuable insights into the adsorption characteristics of the materials for the studied parameters (Table 5). The Freundlich isotherm model, representing heterogeneous surfaces, indicates strong adsorption with high Freundlich constants ( $K_f$ ) for both wheat straw (3.60) and pistachio shell (5.73), with a further increase in adsorption capacity when combined (12.38). The Langmuir isotherm, suggesting monolayer adsorption, demonstrates the highest maximum adsorption capacity ( $q_{max}$ ) for pistachio shell (259.74 mg/g), followed by wheat straw (211.4 mg/g), and the combined system (184.1621 mg/g). The Temkin isotherm, reflecting adsorption energy distribution, exhibits varying Bt values but consistently increasing Kt values for wheat straw (0.55), pistachio shell (0.83), and the combined system (2.03).

### 3.4. Adsorption kinetics

The kinetic modeling results for wheat straw, pistachio shell, and their combination provide insights into the adsorption processes over time (Table 6). The first-order kinetic model, representing a single-layer adsorption mechanism, reveals negative intercepts and slopes for wheat straw, pistachio shell, and the combined system, indicating a decreasing adsorption rate. The equilibrium adsorption capacities ( $q_e$ ) for wheat straw (0.48 mg/g), pistachio shell (0.56 mg/g), and the combined

system (0.5143 mg/g) are relatively low. The second-order kinetic model, implying a multi-layer adsorption process, shows positive intercepts and slopes, reflecting an increasing adsorption rate. The equilibrium adsorption capacities ( $q_e$ ) for wheat straw (27.24 mg/g), pistachio shell (29.58 mg/g), and the combined system (31.37 mg/g) are notably higher compared to the first-order model. The calculated  $q_e^2$  values and high  $R^2$  values (1) suggest an excellent fit to the experimental data, emphasizing the applicability of the second-order kinetic model.

### 3.5. Water quality indices

The study evaluated the effectiveness of different treatment scenarios on water quality parameters, including zinc, total hardness, calcium, manganese, fluorides, nickel, cadmium, nitrates, cyanides, lead, arsenic, TSS, TDS, TN,  $NH_3-N$ , TP, FOG, EC, Cu, surfactants, turbidity, COD, BOD, and TOC. The results demonstrated significant improvements in water quality across multiple parameters in all treatment scenarios compared to raw wastewater. Integrated treatment approaches, particularly the combination of wheat straw and pistachio shells, consistently outperformed individual treatment methods. The integrated treatments resulted in remarkable reductions in the SL<sub>i</sub> values for various parameters, indicating effective removal of contaminants. Parameters such as zinc, manganese, fluorides, nickel, cadmium, nitrates, cyanides, lead, and arsenic exhibited high SL<sub>i</sub> values in raw wastewater, indicating poor water quality. However, all treatment scenarios led to substantial reductions in SL<sub>i</sub> values for these parameters, demonstrating effective removal. Integrated treatment 2, which utilized the effluent from wheat straw treatment as influent in the pistachio shell treatment, showed the lowest SL<sub>i</sub> values for zinc (0.228), manganese (0.974), and fluorides (0.404), indicating successful removal of these contaminants. Additionally, parameters such as total hardness and calcium were completely removed in all treatment scenarios (SLI values of 0), highlighting the efficacy of the treatment methods for these parameters. Other parameters including TSS, TDS, TN,  $NH_3-N$ , TP, FOG, EC, Cu, surfactants, turbidity, COD, BOD, and TOC also exhibited notable improvements across all treatment scenarios, indicating effective removal or reduction of these water quality parameters. The findings demonstrate the overall efficacy of the implemented treatment scenarios for improving water quality. The integrated treatments combining wheat straw and pistachio shells proved to be particularly effective, as they consistently yielded significant reductions in SL<sub>i</sub> values for various parameters (Fig. 3).

The presented results show the WQI values for different water sources, including raw water, water treated with wheat straw, water treated with pistachio shells, and two integrated treatment scenarios (a mix of wheat straw and pistachio shell adsorbents and Series connection of wheat straw and pistachio shell) (Table 7). The WQI is an indicator that provides a comprehensive assessment of water quality based on multiple parameters. The WQI value of 2114.26 for the raw wastewater source clearly denotes water quality that is significantly unsuitable for drinking purposes. This high value suggests the presence of various contaminants and pollutants in the raw water, which may pose risks to human health and the environment. After treatment with wheat straw, the WQI value significantly decreases to 777.61. This reduction demonstrates the effectiveness of the wheat straw treatment in improving water quality by removing or reducing the levels of contaminants. Similarly, the treatment with pistachio shells leads to a further decrease in the WQI value to 750.77. This indicates that pistachio shell treatment contributes to additional improvements in water quality. Both integrated treatment scenarios (a mix of wheat straw and pistachio shell adsorbents and a series connection of wheat straw and pistachio shell) result in even lower WQI values, indicating significant improvements in water quality compared to the raw water source and individual treatment methods. A mix of wheat straw and pistachio shell adsorbents shows a WQI value of 580.44, suggesting a substantial improvement in water quality compared to the raw water source and the individual

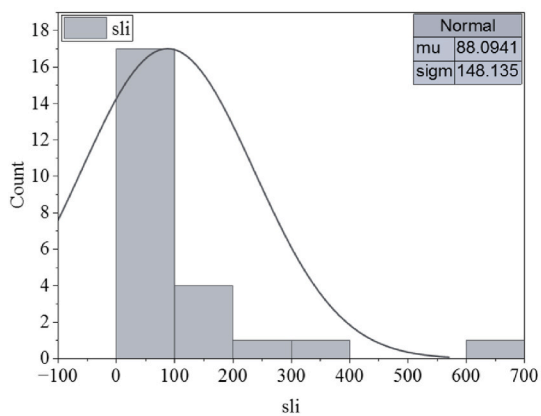
**Table 5**  
Summary of the results from adsorption isotherm analysis.

Isotherm model	Parameter	Value		
		wheat straw	pistachio shell	combined
Freundlich	intercept	0.556	0.758	1.09
	slope	0.903	0.902	0.862
	1/n	0.903	0.902	0.862
	$K_f$	3.599	5.73	12.38
	$R^2$	0.998	0.992	0.998
Langmuir	intercept	0.0047	0.0039	0.0054
	slope	0.294	0.18	0.075
	$q_{max}$ (mg/g)	211.42	259.74	184.16
	$K_L$	0.016	0.0214	0.0727
	$R_L$	0.554	0.484	0.216
	$R^2$	0.9998	0.99889	0.99991
Temkin	intercept	-11.50	-3.58	13.67
	slope	19.32	20.99	21.49
	$B_t$ (J/mol)	19.32	19.32	19.32
	$K_t$ (L/mg)	0.55	0.831	2.029
	$R^2$	0.919	0.929	0.922

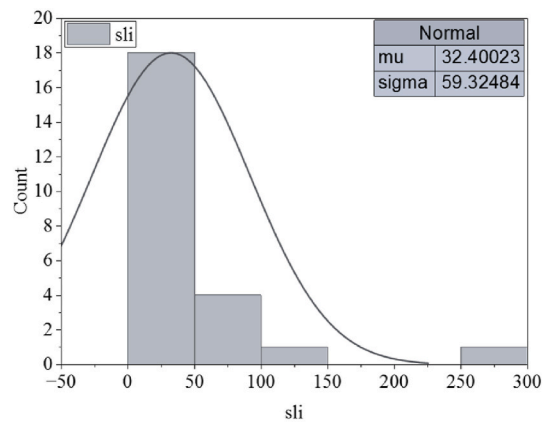
**Table 6**  
Summary of the results from adsorption kinetics analysis.

Kinetic model	Parameter	Value		
		Wheat straw	pistachio shell	combined
first order	intercept	-0.734	-0.58	-0.665
	slope	-0.045	-0.048	-0.046
	$q_e$ (mg/g)	0.4799	0.5598	0.5143
	$k_1$	-0.00074	-0.0008	-0.00077
	$R^2$	0.688	0.675	0.67
second order	intercept	0.0025	0.0025	0.00192
	slope	0.037	0.034	0.032
	$q_e$ (mg/g)	27.24	29.58	31.37
	$q_e^2$	742.05	874.8	983.93
	$K_2$	0.537	0.452	0.529
	$R^2$	1	1	1

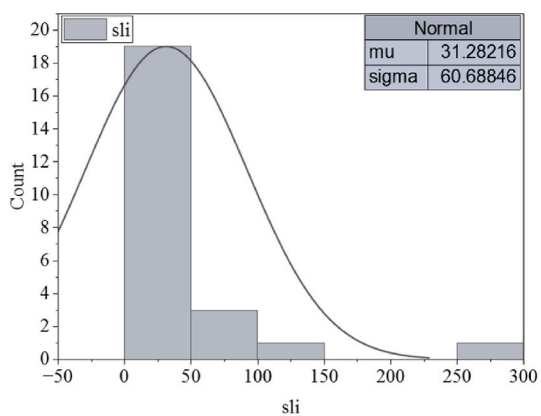




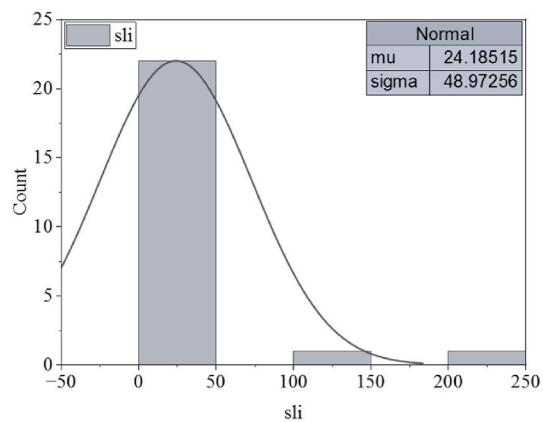
(a)



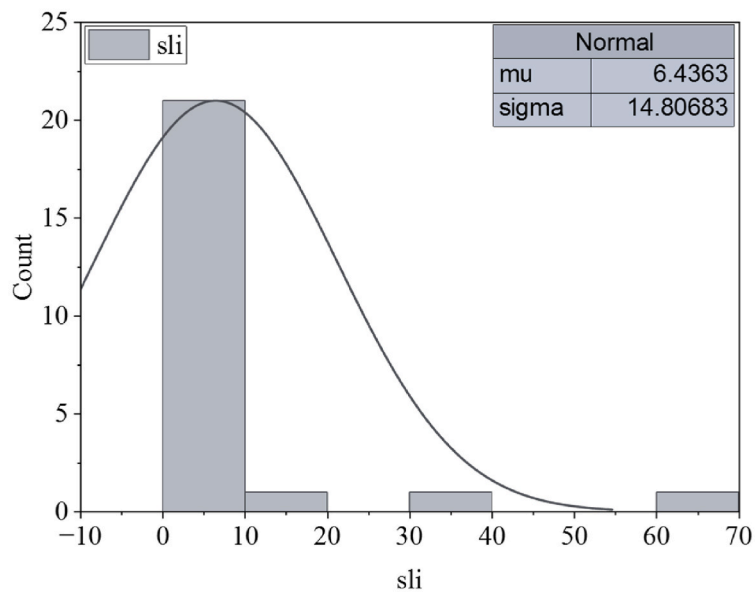
(b)



(c)



(d)



(e)

Fig. 3. Summary of the sub-indices from the investigated parameters.

**Table 7**  
Summary of the aggregated WQIs.

Water source	WQI	Classification
Raw wastewater	2114.26	Unsuitable for Drinking
Wheat Straw	777.61	Unsuitable for drinking
Pistachio Shells	750.77	Unsuitable for drinking
A mix of wheat straw and pistachio shell adsorbents	580.44	Unsuitable for drinking
Series connection of wheat straw and pistachio shell	154.47	Poor Quality

treatment methods. This integrated treatment approach, which combines the benefits of wheat straw and pistachio shell treatments, demonstrates synergistic effects in enhancing water quality. The series connection of wheat straw and pistachio shell exhibits the lowest WQI value of 154.47 among all the treatment scenarios. This indicates that the combination of wheat straw treatment followed by pistachio shell treatment in a sequential manner leads to the most effective water quality improvement. Overall, the results highlight the effectiveness of the implemented treatment scenarios in significantly reducing the WQI values, indicating improvements in water quality. The integrated treatment approaches, particularly the series connection of wheat straw and pistachio shell, show the highest efficacy in achieving substantial improvements in water quality compared to the raw water source and individual treatment methods.

#### 4. Discussion

A study was conducted to assess the effectiveness of different treatment methods in improving water quality by removing various contaminants. The results showed that the Series connection treatment consistently outperformed individual treatments, achieving remarkable removal efficiencies of 100% for parameters such as FOG, TSS, and Turbidity. The Mixture treatment, which combined wheat straw and pistachio shell, also showed advantages over individual treatments, indicating synergistic effects. Several parameters, such as Arsenic, BOD, Cadmium, COD, Fluorides,  $\text{NH}_3\text{-N}$ , and Surfactants, displayed significantly higher removal efficiencies across all treatments, indicating the effectiveness of the methods in targeting a diverse range of contaminants. The Series connection approach demonstrated improvements even for parameters like calcium, cyanides, EC, manganese, nickel, nitrates, TDS, TN, TOC, TP, and total hardness. The study highlighted the importance of treatment integration for comprehensive water quality improvement, with the Series connection being a highly effective and versatile approach. It is important to note that, connecting multiple treatment systems in series enhances removal efficiency by employing a sequential and complementary approach to pollutant removal. Each treatment stage targets specific contaminants, allowing for a step-by-step reduction in pollutant concentrations [32]. In the literature, integrated systems have demonstrated notable effectiveness. For example, in research carried out by Abdel-Fatah, Shaarawy, and Hawash [33], the authors examined the efficacy of an integrated approach for treating municipal wastewater, employing an advanced electro-membrane filtration system. The study demonstrated remarkable removal percentages, with 93% for BOD<sub>5</sub>, 95% for COD, and 100% for phosphates. Statistical analysis using the Tukey HSD test confirmed that the treated effluent, obtained through a series connection of wheat straw and pistachio shell, exhibited significantly different water quality compared to raw wastewater. The application of Bonferroni and Holm corrections for multiple comparisons yielded consistent results with the Tukey HSD test, indicating significant differences between the series connection treatment and raw wastewater. Utilizing the Tukey HSD test along with Bonferroni and Holm corrections for multiple comparisons proved

crucial in comprehending the variations in data derived from diverse sources [34]. In the literature, significant removal efficiencies have been noted when employing agricultural waste for wastewater treatment. For instance, in a study conducted by Xiao-Teng et al. [35], on the adsorption of uranium(VI) from aqueous solutions using modified rice stem, it was found that treating the rice stem with 0.5 mol/L NaOH resulted in the highest uranium removal rate of 94.55%. This outcome was attributed to the abundance of  $\text{SiO}_2$  and nonaromatic esters present on the surface of the modified rice stem. Varsani et al. [36], conducted research on purifying municipal sewage water using agricultural waste materials such as *Arachis hypogaea* shells (AHS), *Triticum aestivum* straw (TAS), and *Gossypium herbaceum* shells (GHS). The effectiveness of the bio-coagulant was assessed by monitoring the reduction in physico-chemical parameters. AHS demonstrated an impressive turbidity removal efficiency of 93.37%, which was supported by both pseudo-first and pseudo-second-order kinetic modeling. The utilization of agricultural waste materials led to significant reductions in key parameters, including solids (by up to 70–80%), dissolved oxygen (DO) (by 50%), and BOD and COD (by up to 90%).

The study also investigated the adsorption characteristics of wheat straw, pistachio shell, and their combination using isotherm models. The Freundlich isotherm model was employed, and it indicated strong adsorption capacity for both wheat straw and pistachio shell. Furthermore, when the two materials were combined, there was a further increase in adsorption capacity. The Langmuir isotherm model was also applied, and it revealed that pistachio shells had the highest maximum adsorption capacity, followed by wheat straw and the combined system. On the other hand, the Temkin isotherm model displayed varying adsorption energy distribution values. However, it consistently showed increasing values for wheat straw, pistachio shell, and the combined system. These results suggested that the combination of wheat straw and pistachio shell enhanced the adsorption capacity, making it a promising approach for water treatment. In terms of kinetic modeling, the study employed the first-order and second-order kinetic models. The first-order kinetic model indicated a decreasing adsorption rate for wheat straw, pistachio shell, and the combined system. Conversely, the second-order kinetic model showed an increasing adsorption rate and notably higher equilibrium adsorption capacities compared to the first-order model. The examination of isotherms allowed for a detailed assessment of the equilibrium sorption capacities and the affinity of the bio-functionalized biomass for pollutants in wastewater [37]. Simultaneously, kinetics studies provided essential information on the rate at which the adsorption process occurs, aiding in the design and optimization of efficient wastewater treatment strategies using bio-functionalized biomass [38]. This combined approach enhanced the overall understanding of the adsorption dynamics and performance of the treatment system, contributing to the advancement of sustainable and effective wastewater treatment methodologies [39,40]. In Mu et al.'s [41], investigation into the adsorption of Pb(II) from aqueous solutions using wheat straw biochar, it was noted that the Langmuir isotherm model exhibited the most favorable correlation for Pb<sup>2+</sup> adsorption, suggesting a chemical monolayer adsorption mechanism. The adsorption capacity ( $q_m$ ) showed an increase with rising temperature, reaching 149.701 mg/g for CS (chemically modified straw) and 44.663 mg/g for NS (natural straw) at 35 °C, respectively.

Moreover, the study evaluated the effectiveness of different treatment scenarios on various water quality parameters based on water quality sub-indices. Significant improvements were observed across multiple parameters in all treatment scenarios compared to raw wastewater. Integrated treatment approaches, particularly the combination of wheat straw and pistachio shells, consistently outperformed individual treatment methods. The integrated treatments resulted in substantial reductions in the SI values for various parameters, indicating effective removal of contaminants. Parameters such as zinc, manganese, fluorides, nickel, cadmium, nitrates, cyanides, lead, and arsenic exhibited high SI values in raw wastewater but showed significant reductions in all

treatment scenarios. Parameters such as TSS, TDS, TN, NH<sub>3</sub>-N, TP, FOG, EC, Cu, surfactants, turbidity, COD, BOD, and TOC exhibited notable improvements. The findings demonstrated the overall efficacy of the treatment scenarios for improving water quality, with the combination of wheat straw and pistachio shells being particularly effective. The WQI values were calculated for different water sources and treatment scenarios. It is important to note that, a WQI serves as a comprehensive metric, condensing diverse water quality parameters into a single value, facilitating a simplified and accessible assessment of overall water quality [42]. The WQI value for raw water indicated poor water quality, but it significantly decreased after treatment with wheat straw and pistachio shells. The integrated treatment scenarios resulted in even lower WQI values, indicating substantial improvements in water quality compared to raw water and individual treatments. Integrated treatment 2, which involved wheat straw treatment followed by pistachio shell treatment, showed the lowest WQI value among all treatment scenarios, indicating the most effective water quality improvement. However, it has been observed in the literature that the dosage concentration can play a significant role in the efficacy of agricultural waste biomass for wastewater treatment. Guo et al. [43], explored the impact of alkali treatment of wheat straw on the adsorption of Cu(II) under acidic conditions. They found that increasing the concentration of the adsorbent from 0.5 to 5 g/L led to a notable enhancement in the Cu(II) removal rate for alkali-treated wheat straw (AWS), rising from 15.6% to 92.7%, whereas the removal rate for untreated wheat straw (UWS) increased from 10.3% to 45.2%. Subsequent to reaching the critical dosage of 5 g/L, the increase in Cu(II) removal rate occurred gradually. Overall, the study demonstrated the effectiveness of different treatment methods in improving water quality by removing various contaminants. The integration of wheat straw and pistachio shells showed synergistic effects and proved to be particularly effective in enhancing water quality. The results emphasized the importance of integrated treatment strategies for achieving comprehensive water quality improvement and providing safe and clean water resources.

## 5. Conclusion

The potential applicability of bio-functionalized adsorbent from wheat straw and pistachio shell bio-mass for wastewater treatment has been investigated. The investigation involved several treatment setups including the treatment system with bio-functionalized wheat straw alone, pistachio shell alone, a mix of wheat straw and pistachio shell as well as a series connection of the wheat straw treatment setup followed by the pistachio shell treatment setup. From the results, it was observed that the series connection treatment demonstrated exceptional removal efficiencies for critical parameters such as fat, oil, and grease, total suspended solids, and turbidity. The Mixture treatment exhibited synergistic effects in removing contaminants like Arsenic, BOD, cadmium, COD, fluorides, ammonia nitrogen, and surfactants. Specifically, the series treatment achieved nearly complete removal (approximately 100%) for fat, oil, and grease, turbidity, and total suspended solids. Wheat straw and pistachio shell treatments individually achieved removal efficiencies ranging from 41.3% to 83.3% and 43.3%–89.1%, respectively. Statistical analyses confirmed the significance of the observed differences, while isotherm and kinetic models provided valuable insights into the adsorption characteristics. The Freundlich constants ranged from 3.6 to 12.38, indicating strong adsorption capacities of the bio-functionalized biomasses. The integrated treatments consistently outperformed individual treatments, as demonstrated by the WQI values. The WQI values ranged from 2114.26 for raw wastewater, classified as “unsuitable for drinking,” to 154.47 for the series connection of wheat straw and pistachio shell, indicating a significant improvement in water quality. The inclusion of additional treatment setups, particularly in a series configuration, is expected to significantly improve the water quality, potentially elevating it to an excellent status. In essence, the study highlights the pivotal role of treatment integration,

particularly through the Series connection, in comprehensively addressing a diverse range of water quality challenges. The findings emphasize the practical implications for water treatment systems, underscoring the potential of integrated strategies to efficiently remove contaminants and ensure the provision of safe and clean water resources. Further investigations should encompass a wider range of contaminants and consider the influence of varying operational conditions, such as flow rates and contact times. Long-term studies are also necessary to assess the stability and durability of the integrated treatment systems. Additionally, comprehensive cost-benefit analyses and life cycle assessments should be conducted to evaluate the economic feasibility and environmental impacts of the proposed integrated approaches. Future studies could also explore the potential of incorporating additional biomaterials or exploring alternative treatment configurations to further enhance the removal efficiencies and broaden the scope of applications.

## CRedit authorship contribution statement

**Timoth Mkilima:** Writing – original draft, Supervision, Methodology, Investigation, Formal analysis, Conceptualization. **Yerkebulan Zharkenov:** Resources, Project administration, Investigation, Funding acquisition. **Aisulu Abduova:** Resources, Investigation. **Nursulu Sarypbekova:** Resources, Investigation. **Kamilya Kirgizbayeva:** Resources, Investigation. **Ilyyas Zhumadilov:** Resources, Investigation. **Farida Kenzhekulova:** Resources, Investigation. **Mukhtarov Abil-khas:** Resources, Investigation. **Shyngys Zharassov:** 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.

## References

- [1] N. Patel, M. Feofilovs, D. Blumberga, Agro biopolymer: a sustainable future of agriculture – state of art review, *Environ. Clim. Technol.* 26 (2022) 499–511, <https://doi.org/10.2478/rtuect-2022-0038>.
- [2] M. Waqas, S. Hashim, U.W. Humphries, S. Ahmad, R. Noor, M. Shoaib, A. Naseem, P.T. Hlaing, H.A. Lin, Composting Process. *Agric. Waste Manag.: Compr. Rev. Process.* 11 (2023) 731, <https://doi.org/10.3390/pr11030731>.
- [3] H.J. Zahid, E. Robinson, R.L. Kelly, Agriculture, population growth, and statistical analysis of the radiocarbon record, *Proc. Natl. Acad. Sci.* 113 (2016) 931–935, <https://doi.org/10.1073/pnas.1517650112>.
- [4] M. Katiyar, Solid Waste Management, *RIET-IJSET Int. J. Sci. Eng. Technol.* 3 (2016) 117, <https://doi.org/10.5958/2395-3381.2016.00015.0>.
- [5] R. Yevich, J.A. Logan, An assessment of biofuel use and burning of agricultural waste in the developing world, *Global Biogeochem. Cycles* 17 (2003), <https://doi.org/10.1029/2002GB001952>.
- [6] FAO, The Future of Food and Agriculture – Alternative Pathways to 2050, 2018. <http://www.fao.org/3/18429EN/i8429en.pdf>.
- [7] A.I. Adetunji, A.O. Olaniran, Treatment of industrial oily wastewater by advanced technologies: a review, *Appl. Water Sci.* 11 (2021) 98, <https://doi.org/10.1007/s13201-021-01430-4>.
- [8] A.D.M. de Medeiros, C.J.G. da Silva Junior, J.D.P. de Amorim, I.J.B. Durval, A.F. de Santana Costa, L.A. Sarubbo, Oily Wastewater Treatment: Methods, Challenges, and Trends, *Processes*, 2022, <https://doi.org/10.3390/pr10040743>.
- [9] E. Neczaj, A. Grosser, Circular economy in wastewater treatment plant—challenges and barriers, in: *EWaS3 2018, MDPI, Basel Switzerland*, 2018, p. 614, <https://doi.org/10.3390/proceedings2110614>.
- [10] M. Farooq, N. Gogoi, M. Pisante, Sustainable Agriculture and the Environment, Elsevier, 2023, <https://doi.org/10.1016/C2020-0-03402-X>.
- [11] B. Koul, M. Yakob, M.P. Shah, Agricultural waste management strategies for environmental sustainability, *Environ. Res.* 206 (2022) 112285, <https://doi.org/10.1016/j.envres.2021.112285>.

- [12] J.W. Agger, B. Zeuner, Bio-based surfactants: enzymatic functionalization and production from renewable resources, *Curr. Opin. Biotechnol.* (2022), <https://doi.org/10.1016/j.copbio.2022.102842>.
- [13] T. Tufail, F. Saeed, M. Afzaal, H.B.U. Ain, S.A. Gilani, M. Hussain, F.M. Anjum, Wheat straw: a natural remedy against different maladies, *Food Sci. Nutr.* (2021), <https://doi.org/10.1002/fsn3.2030>.
- [14] I.G. Shaikhiev, N.V. Kraysman, S.V. Sverguzova, Review of pistachio (pistacia) shell use to remove pollutants from aqua media, *Biointerface Res. Appl. Chem.* 13 (2022) 389, <https://doi.org/10.33263/BRIAC134.389>.
- [15] A.A. Al-Gheethi, Q.M. Azhar, P. Senthil Kumar, A.A. Yusuf, A.K. Al-Buriah, R.M. S. Radin Mohamed, M.M. Al-shaibani, Sustainable approaches for removing Rhodamine B dye using agricultural waste adsorbents: a review, *Chemosphere* (2022), <https://doi.org/10.1016/j.chemosphere.2021.132080>.
- [16] N.N. Rudi, M.S. Muhammad, L. Te Chuan, J. Alipal, S. Omar, N. Hamidon, N. H. Abdul Hamid, N. Mohamed Sunar, R. Ali, H. Harun, Evolution of Adsorption Process for Manganese Removal in Water via Agricultural Waste Adsorbents, *Heliyon*, 2020, <https://doi.org/10.1016/j.heliyon.2020.e05049>.
- [17] S. Mallakpour, F. Motirasoul, Bio-functionalizing of  $\alpha$ -MnO<sub>2</sub> nanorods with natural l-amino acids: a favorable adsorbent for the removal of Cd(II) ions, *Mater. Chem. Phys.* 191 (2017) 188–196, <https://doi.org/10.1016/j.matchemphys.2017.01.040>.
- [18] A. Francesco, L. Blandón, M. Vázquez, P. Petkova, J. Morató, A. Pfeifer, T. Heinze, E. Mendoza, T. Tzanov, Enzymatic functionalization of cork surface with antimicrobial hybrid biopolymer/silver nanoparticles, *ACS Appl. Mater. Interfaces* (2015), <https://doi.org/10.1021/acsami.5b01670>.
- [19] G.F. Coelho, A.C. Gonçalves Jr., C.R.T. Tarley, J. Casarin, H. Naecke, M. A. Francziskowski, Removal of metal ions Cd (II), Pb (II), and Cr (III) from water by the cashew nut shell Anacardium occidentale L, *Ecol. Eng.* 73 (2014) 514–525, <https://doi.org/10.1016/j.ecoleng.2014.09.103>.
- [20] F. Bin Abdurrahman, M. Akter, M.Z. Abedin, Dyes removal from textile wastewater using orange peels, *Int. J. Sci. Technol. Res.* 2 (2013) 47–50.
- [21] S. Kamsonlian, S. Suresh, C.B. Majumder, S. Chand, Characterization of banana and orange peels: biosorption mechanism, *Int. J. Sci. Technol. Manag.* 2 (2011) 1–7.
- [22] R. Ebrahimi, A. Maleki, B. Shahmoradi, H. Daraei, A.H. Mahvi, A.H. Barati, A. Eslami, Elimination of arsenic contamination from water using chemically modified wheat straw, *Desalin. Water Treat.* 51 (2013) 2306–2316, <https://doi.org/10.1080/19443994.2012.734675>.
- [23] D. Bozic, M. Gorgievski, V. Stankovic, M. Kacic, S. Dimitrijevic, V. Conic, Biosorption of lead ions from aqueous solutions by beech sawdust and wheat straw, *Chem. Ind. Chem. Eng. Q.* 27 (2021) 21–34, <https://doi.org/10.2298/CICEQ191113021B>.
- [24] K. Rambabu, G. Bharath, F. Banat, P.L. Show, Biosorption performance of date palm empty fruit bunch wastes for toxic hexavalent chromium removal, *Environ. Res.* (2020), <https://doi.org/10.1016/j.envres.2020.109694>.
- [25] A. Jalali, F. Mirnezami, M. Lotfi, M. Shafiee, A.H. Mohammadi, Biosorption of lead ion from aqueous environment using wheat stem biomass, *Desalin. Water Treat.* 233 (2021) 98–105, <https://doi.org/10.5004/dwt.2021.27518>.
- [26] C.H. Weng, Y.T. Lin, D.Y. Hong, Y.C. Sharma, S.C. Chen, K. Tripathi, Effective removal of copper ions from aqueous solution using base treated black tea waste, *Ecol. Eng.* (2014), <https://doi.org/10.1016/j.ecoleng.2014.03.053>.
- [27] A. Said, D.K. Stevens, G. Sehlke, An innovative index for evaluating water quality in streams, *Environ. Manag.* 34 (2004) 406–414, <https://doi.org/10.1007/s00267-004-0210-y>.
- [28] K. Meiramkulova, A.A. Zorpas, D. Orynbekov, M. Zhumagulov, G. Saspugayeva, A. Kydyrbekova, T. Mkilima, V.J. Inglezakis, The effect of scale on the performance of an integrated poultry slaughterhouse wastewater treatment process, *Sustainability* 12 (2020) 4679, <https://doi.org/10.3390/su12114679>.
- [29] K. Meiramkulova, A. Kydyrbekova, D. Devrshov, U. Nurbala, A. Tuyakbayeva, S. Zhangazin, R. Ualiyeva, V. Kolpakova, Y. Yeremeyeva, T. Mkilima, Comparative analysis of natural and synthetic zeolite filter performance in the purification of groundwater, *Water* 15 (2023) 588, <https://doi.org/10.3390/w15030588>.
- [30] A. Bhatnagar, P. Devi, M.P. George, Impact of mass bathing and religious activities on water quality index of prominent water bodies: a multilocation study in Haryana, India, *Int. J. Ecol.* (2016), <https://doi.org/10.1155/2016/2915905>.
- [31] A.H.M.J. Alobaidy, H.S. Abid, B.K. Maulood, Application of water quality index for assessment of dokan lake ecosystem, kurdistan region, Iraq, *J. Water Resour. Protect.* 2 (2010) 792–798, <https://doi.org/10.4236/jwarp.2010.29093>.
- [32] K. Meiramkulova, A. Temirbekova, G. Saspugayeva, A. Kydyrbekova, D. Devrshov, Z. Tulegenova, K. Aubakirova, N. Kovalchuk, A. Meirbekov, T. Mkilima, Performance of a combined treatment approach on the elimination of microbes from poultry slaughterhouse wastewater, *Sustainability* 13 (2021) 3467, <https://doi.org/10.3390/su13063467>.
- [33] M.A. Abdel-Fatah, H.H. Shaarawy, S.I. Hawash, Integrated treatment of municipal wastewater using advanced electro-membrane filtration system, *SN Appl. Sci.* 1 (2019) 1153, <https://doi.org/10.1007/s42452-019-1178-9>.
- [34] S.T. Mala, B.R. Kiran, One-way ANOVA, Tukey HSD, scheffe, Bonferroni and Holm multiple comparison tests for physico-chemical parameters in four water bodies of davangere district, Karnataka, *Int. J. Life Sci. Pharma Res.* (2021), <https://doi.org/10.22376/ijpbs/lpr.2021.11.2.L66-73>.
- [35] Z. Xiao-teng, J. Dong-mei, X. Yi-qun, C. Jun-chang, H. Shuai, X. Liang-shu, Adsorption of uranium(VI) from aqueous solution by modified rice stem, *J. Chem.* (2019) 1–10, <https://doi.org/10.1155/2019/6409504>, 2019.
- [36] V.G. Varsani, S.J. Vyas, V. Parmar, D. Dudhagara, S. Gamit, D. Ali, V.K. Yadav, D. K. Sahoo, A. Patel, Efficient and eco-friendly treatment of wastewater through sustainable purification using agricultural waste and coagulation kinetic modelling, *Front. Environ. Sci.* 11 (2024), <https://doi.org/10.3389/fenvs.2023.1280125>.
- [37] N.S. Ali, N.M. Jabbar, S.M. Alardhi, H.S. Majdi, T.M. Albayati, Adsorption of methyl violet dye onto a prepared bio-adsorbent from date seeds: isotherm, kinetics, and thermodynamic studies, *Heliyon* 8 (2022) e10276, <https://doi.org/10.1016/j.heliyon.2022.e10276>.
- [38] Z. Raji, A. Karim, A. Karam, S. Khaloufi, Adsorption of heavy metals: mechanisms, kinetics, and applications of various adsorbents in wastewater remediation—a review, *Waste* 1 (2023) 775–805, <https://doi.org/10.3390/waste1030046>.
- [39] J. Wang, X. Guo, Adsorption kinetics and isotherm models of heavy metals by various adsorbents: an overview, *Crit. Rev. Environ. Sci. Technol.* 53 (2023) 1837–1865, <https://doi.org/10.1080/10643389.2023.2221157>.
- [40] L. Zhang, Y. Zeng, Z. Cheng, Removal of heavy metal ions using chitosan and modified chitosan: a review, *J. Mol. Liq.* 214 (2016) 175–191, <https://doi.org/10.1016/j.molliq.2015.12.013>.
- [41] R.M. Mu, M.X. Wang, Q.W. Bu, D. Liu, Y.L. Zhao, Adsorption of Pb(II) from aqueous solutions by wheat straw biochar, *IOP Conf. Ser. Earth Environ. Sci.* (2018), <https://doi.org/10.1088/1755-1315/191/1/012041>.
- [42] M.G. Uddin, S. Nash, A.I. Olbert, A review of water quality index models and their use for assessing surface water quality, *Ecol. Indic.* 122 (2021) 107218, <https://doi.org/10.1016/j.ecolind.2020.107218>.
- [43] Y. Guo, W. Zhu, G. Li, X. Wang, L. Zhu, Effect of alkali treatment of wheat straw on adsorption of Cu(II) under acidic condition, *J. Chem.* (2016) 1–10, <https://doi.org/10.1155/2016/6326372>, 2016.