



Eco-friendly sustainable biofilters media for UASB effluent post-treatment in agrofood industry wastewater using design of experiments and LCA

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Abstract

This study evaluates and compares sustainable, low-cost biofilter media, specifically chitosan and *Phragmites australis* biochar, with commercial activated carbon to remove chemical oxygen demand (COD) and phenol from agro-food industry wastewater. The primary objective is to identify an effective and eco-friendly alternative to conventional adsorbents for the post-treatment of effluents from Upflow Anaerobic Sludge Blanket (UASB) reactors. COD and phenol are targeted due to their environmental significance; COD reflects overall organic pollution, while phenol is a toxic, persistent compound in oily industrial wastewater. Multi-level factorial design experiments optimized using three types of adsorbent materials with different doses to improve the Biofilter performance. COD removal and phenol were studied as a function of four experimental parameters: adsorbent materials, dose, contact time, and wastewater type. To minimize the number of experiments, MINITAB Version 19 software conducted the experiments using a multi-level full factorial design, reducing the total number of experimental runs required while still capturing the interactions and effects of the different factors involved. The characterization investigation was carried out using X-ray diffractometry (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and Brunauer–Emmett–Teller (BET). The optimal conditions achieved a composite desirability of 0.9872, indicating a near-ideal balance for both responses. For COD removal, the maximum rate of 98.3721% was achieved under the optimal conditions with *Phragmites australis* biochar (Adsorbent Material 2), UASB effluent (Wastewater Type 2), a contact time of 90 min, and a dose of 6.5 g/L, yielding a desirability value of 0.97463. The maximum rate of 86.6766% for phenol removal was also attained under the same optimal conditions, yielding a desirability value of 1.0000, representing perfect optimization for phenol removal. A Life Cycle Assessment (LCA) was conducted to evaluate the environmental impacts associated with the treatment of UASB effluent and Arma wastewater using the three different adsorbent materials. The *Phragmites australis* biochar offers the most environmentally sustainable option for wastewater treatment. It significantly reduces greenhouse gas emissions, resource depletion, toxicity impacts, and energy use compared to Activated Carbon and Chitosan. This research is consistent with the United Nations Sustainable Development Goals (SDGs), namely SDG 6 (Clean Water and Sanitation) and SDG 12 (Responsible Consumption and Production). Our findings have far-reaching implications for large-scale wastewater treatment, offering a greener and more sustainable future.

Keywords Sustainable · Biotreatment · Chitosan · Biochar · Phenol · Chemical oxygen demand · Factorial design · Agro-food industrial wastewater · Milkmaid wastewater

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Introduction

An appropriate and comprehensive strategy is required to manage the effluents produced by the various agro-food industries, which pose a hazard to the environment. Rapid and effective treatment and utilization of these wastes is required due to the increasing stringency of legislation. Not only that, but the UASB reactor's effluent doesn't meet the criteria set by different environmental organizations for the release of such pollutants (Chernicharo et al. 2015; Tandukar et al. 2007). The residual organic matter in the effluent of the UASB reactor that treats wastewater is sufficiently high. Additionally, the effluent contains a high concentration of pathogens and nutrients. The selection of filter media is a critical component of the biofilter, in addition to the aeration process and backwash system (El Shahawy and Heikal 2018b; Heikal and El Shahawy 2019).

Furthermore, the filter media selection influences the rate of oxygen substrate transfer and the hydraulic characteristics (Loh et al. 2021). Granular activated carbon (GAC) (Dos Santos et al. 2022), quartz sand (Shaikh and Ahammed 2022), and anthracite (Loh et al. 2021) are the frequently used conventional filter media in biofilter systems. The use of organic or waste-based materials as filter media in biofiltration treatment has long piqued the curiosity of researchers (Umar et al. 2025).

The growing pressures of urbanization, population increase, and global drought have intensified the demand for water resources, leading to severe pollution in water bodies such as lakes, rivers, and coastal areas (Wang et al. 2024). This pollution, especially from industrial discharge, poses significant risks to ecosystems and human health and highlights the need for effective water treatment solutions (Periyasamy 2024). Phenol, a persistent organic pollutant with high toxicity, exemplifies such industrial pollutants and is particularly challenging to remove due to the stability of its benzene structure (Fisher et al. 2025).

The agro-food industry contributes to water pollution, producing effluents that often do not meet discharge standards. Effluents from UASB reactors used in treating agro-food wastewater, such as dairy or meat processing effluents, frequently contain high levels of organic matter and residual nutrients that require further treatment to meet environmental discharge standards (Halalsheh et al. 2010; Zhang et al. 2022). This underscores the need for effective post-treatment to achieve compliance with effluent disposal guidelines and ensure safe reuse, especially in agriculture (El Shahawy and Heikal 2018a; El Shahawy et al. 2024). Organic and waste materials, such as wood chips, natural fibers, and biochar, are increasingly being recognized as potential alternatives to traditional filter media like sand, activated carbon, and anthracite

in biofiltration systems (Umar et al. 2025). While conventional media are effective, they often come with high costs, limited sustainability, and environmental challenges related to production and disposal. By contrast, organic waste materials offer a sustainable, cost-effective solution, leveraging locally available resources and reducing solid waste by repurposing it in treatment (Abdel-Shafy & Mansour 2018; Abotaleb et al. 2024).

However, despite the promising potential of organic media, significant gaps remain in understanding their performance consistency, durability, and adaptability to varying wastewater compositions, particularly for complex agro-food industry effluents, which can vary greatly in their chemical makeup (Han et al. 2019). While materials such as activated carbon have established efficacy and known parameters for pollutant removal, organic alternatives have yet to be thoroughly studied under different treatment conditions (Zhang et al. 2022). Variables such as contact time, material dosing, and interaction effects with wastewater types are often less predictable for organic materials, leading to inconsistent pollutant removal outcomes and potential challenges with media clogging and degradation (Mishra et al. 2024).

This study addresses this gap by systematically evaluating two eco-friendly materials, chitosan, and *Phragmites australis* biochar, against activated carbon, focusing on their ability to remove COD and phenol from UASB-treated agro-food wastewater. The study specifically investigates the impact of adsorbent type, dose, contact time, and wastewater source on treatment efficiency using a multilevel full factorial design. Before and after treatment, material characterization was performed using XRD, SEM, EDX, and FTIR analyses to assess structural and chemical changes. The study aims to inform the design of continuous, viable, green, sustainable biofiltration systems suitable for large-scale implementation, ultimately contributing to improved environmental management and resource recovery.

Materials and methods

Adsorbents preparation

Chitosan synthesis

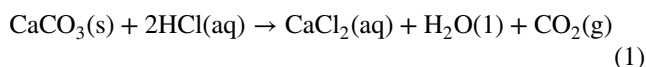
Chitosan preparation is carried out in three stages:

Deproteinization stage: dried shrimp shells were added to sodium hydroxide (NaOH) 2%wt solution, heated up to 60 °C for an hour, filtered, and washed up to neutrality.

Decarbonation was performed by dissolving calcium carbonate (CaCO₃) by washing the resulting mixture from the first step with 7% hydrochloric acid (HCl) at room temperature for 4 h (for calcium carbonate removal as carbon



dioxide) as shown in Eq. (1). The mixture (chitin) was washed until neutral.



A decatalyzing step was performed to extract chitosan from chitin. The resulting mixture from the second step was added to sodium hydroxide (NaOH) 50% wt solution, heated to 120 °C, and stirred for 2 h. Then, the resulting chitosan was filtered and washed till neutral.

Preparation of *Phragmites australis* biochar and activated carbon

Phragmites australis (*Pa*) biomass is widespread and the dominant plant species in many aquatic ecosystems. It is also reported to contain a high amount of lignin and cellulose. *Pa* is a widely spread grass in North Delta, Egypt, growing as an aggressive and invasive plant around lakes, ponds, river shores, and canals (El Shahawy and Heikal 2018a, b).

Collecting *P. australis* from the Suez Canal University Veterinary Experimental Farm in Ismailia, Egypt, the precursor was rinsed with distilled water to remove surface-adhered dirt, impurities, and water-soluble materials. Then it was dried. The dried *P. australis* was ground in a laboratory mill and sieved to obtain particles 1–2 mm in size. The mass was then transferred to a pyrolysis reactor and heated slowly to 550 °C, where it was held for 2 h before being cooled to room temperature. The pyrolyzed product was washed repeatedly with distilled water until a neutral pH was obtained and then dried overnight in a dry oven at 110 °C. The dried sample was ground and sieved to a 200 mesh particle size by standard sieves (Model Φ200) before storage in a desiccator for later experimental use (Tao et al. 2020).

Wastewater sources and analysis

The Arma firm supplied industrial wastewater samples in Ismailia, Egypt, as well as wastewater quality parameters. All of the analyses were carried out using standard methodologies for water inspection. A gravimetric method was employed to determine the TDS of the filtrate. The COD was determined using standard procedures for water testing. The pH of the initial water (that was being tested) was adjusted using either hydrochloric acid (HCl) or sodium hydroxide

(0.1 M). We exclusively utilize chemicals of the highest quality, which are purchased from the local market in Egypt.

Daily, a substantial quantity of buffaloes was transported for cleaning before milking at a buffalo washer at the Suez Canal University Veterinary Experimental Farm in Ismailia, Egypt. The effluent wastewater collected from the buffalo washer was collected in an underground tank, and then primary and secondary treatment processes were performed on the wastewater. Samples were taken from the outlet of the UASB unit (secondary treatment) and then transported to Suez Canal University's Centre for Environmental Studies and Consultants in Ismailia, Egypt. Study the parameters affecting the bio-sorbent's capacity for COD and phenol removal from wastewater. As per the guidelines established by the American Public Health Association for the analysis of water and wastewater (Apha 1985), biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), total dissolved solids (TDS), pH, color, and turbidity of wastewater were determined, as shown in Table 1.

Natural buffalo wastewater with different properties was used from the Suez Canal University veterinary experimental Farm in Ismailia, Egypt. Figure 1 shows this. Underground tanks collected the effluent wastewater (capacity 8m³).

The pH meter was used to record the pH readings (AD1000). Raw and processed water analysis for COD concentrations has been carried out using atomic absorption techniques (AAS) utilizing the ZEEnitu 700P-Analytik Jena-Germany flammatic absorption spectrometer. Table 2 presents a detailed list of materials used in the experimental study, highlighting their sources. Hydrochloric acid and sodium hydroxide, both essential chemical reagents, were supplied by Alpha Chemika, a chemical company based in Egypt. Furthermore, *Phragmites australis*, a type of reed, was harvested from a local farm in Ismailia, and chitosan, a biopolymer, was procured from the local market in the same area.

Factorial design and optimization

In the current study, two types of organic pollutants, COD and phenol, were absorbed from two types of wastewater (domestic and industrial) using biosorbent materials such as *Phragmites australis* biochar and chitosan. They compared together under the effect of parameters such as (contact time, adsorbent dose, supporting material type, and wastewater

Table 1 Wastewater characteristics

Pollutants	COD	BOD	Phenol	TSS	TDS	Turbidity	Color	pH
Domestic ww	603	173.55	18	81.07	298.28	59.28	67.28	7.61
Oily ww	1396.25	862.65	22.88	77.53	1408	605.9	1730	7.88





Fig. 1 **a** Arma factory for industrial oily wastewater. **b** Effluent wastewater from the UASB unit. **c** The modified UASB reactor: inoculating the immobilized *Phragmites australis* biochar with *Streptomyces hydrogenans*

Table 2 Company for materials used

No	Materials	Company
2	HCL, NaOH	Alpha Chemika, Egypt
3	<i>Phragmites australis</i>	Local farm in Ismailia, Egypt
4	Chitosan	Local market, Ismailia, Egypt

type). Table 3 shows twelve (24) batch experiments in this research. There are four input variables: Biochar dose (0.50 and 6.50 g/L), Contact Time (20 and 90 min), wastewater type (1, 2) stands for (Arma wastewater, UASB effluent), and adsorbent material (0, 1, 2) stands for (Activated carbon, Chitosan, *Phragmites australis* Biochar), respectively. All

Table 3 Four-variable full-factorial design matrix with experimental responses

Run	Real values					
	Material dose	Wastewater type	Contact time	Supporting material	COD RR%	Phenol RR%
1	6.5	2	90	2	96.2	86.2
2	0.5	1	90	0	91.6	59.3
3	6.5	2	20	1	93.8	70.7
4	6.5	1	90	1	80.4	63.5
5	0.5	2	90	1	96.0	75.4
6	6.5	1	20	0	79.7	70.7
7	0.5	2	90	0	62.6	76.0
8	0.5	1	90	1	76.9	57.5
9	0.5	1	20	2	80.5	71.3
10	0.5	2	20	1	92.9	70.7
11	6.5	1	90	0	79.5	68.9
12	6.5	1	20	1	77.3	47.3
13	6.5	1	20	2	87.8	74.9
14	6.5	2	90	0	78.5	75.4
15	0.5	2	90	2	99.3	71.9
16	0.5	2	20	2	80.9	58.7
17	6.5	2	20	2	93.2	83.8
18	6.5	2	20	0	96.7	75.4
19	6.5	1	90	2	85.3	73.1
20	6.5	2	90	1	80.4	63.5
21	0.5	1	90	2	88.8	55.1
22	0.5	2	20	0	93.3	67.7
23	0.5	1	20	0	83.6	50.3
24	0.5	1	20	1	78.9	64.1



the possible ways that the variables could be combined were studied in the experimental matrix.

The parameters involved in the adsorption experiments were optimized by multilevel full factorial design using the statistical software MINITAB (Version 21) of Minitab. All the experiments were carried out in random order.

Batch adsorption experiments

The equilibrium method was used to conduct batch adsorption studies involving 200 mL of wastewater at room temperature. A 250 rpm agitation speed was used to shake the samples, and the pH of the wastewater was adjusted as required using nutrient buffer solutions. Finally, to detect the adsorption capacity, the treated wastewater was filtered through a Whatman 42 filter paper to separate the adsorbent from the wastewater. For the analysis of the treated wastewater sample, the percentage removal (R%) was calculated by the following Eqs. (2) and (3):

$$\text{Removal(R)\%} = ((C_0 - C_e)/C_0) \times 100 \quad (2)$$

$$Q_e = (C_0 - C_e) \times V/W \quad (3)$$

C_0 and C_e denote the initial and final concentrations of the contaminants in the solution, respectively. Q_e (mg/g) is the solid's equilibrium adsorption capacity. The dried adsorbent used during the experiment weighs W (g), while V (mL) is the volume of solution contaminated with COD and phenol. COD concentrations were determined colorimetrically. A 2.5 mL standard or sample was added to the digestion tube containing 3.5 mL H_2SO_4/Ag_2SO_4 and 1.5 mL digestion solution. The tubes were tightly capped, swirled several times to mix thoroughly, and incubated at 150 °C for 2 h. A blank sample containing distilled water was also prepared. After incubation, tubes were allowed to cool, inverted twice, and the particles were settled before measuring absorbance at 600 nm. The spectrophotometer (Ceci/3000) was zeroed using the blank tube. Absorbance against the known Potassium hydrogen phthalate (KHP) standard concentrations was plotted to get a standard curve, from which the mathematical equation was determined to calculate the COD. Phenol Measurement Method (Folin–Ciocalteu Method) (Hazreen-Nita et al. 2022).

A sample of 0.5 mL was added to a test tube. 2.5 mL of Folin reagent (0.2 N) was added to the sample and left for 5 min in the dark. 2 mL of Na_2CO_3 (7.5%) was added to the tube and left for 60 min in the dark, then measured on a spectrophotometer at $\lambda=765$ nm. Note: Gallic acid was used as a phenolic compound, the standard for the standard calibration curve at concentrations (10 mg/L: 100 mg/L), where x and y represent Gallic acid concentration (mg/L) and absorbance at 765 nm. As mentioned before (2.4. Factorial design and

Optimization), twenty-four experiments were conducted in this study. Table 3 displays the mean COD removal effectiveness, calculated from the experimental matrix of all conceivable combinations between variable studies.

Materials characterization

The chemical studies of *Phragmites australis* biochar (PAB) were conducted using an “Axion” X-ray fluorescence spectrometer equipped with a 1-kW wavelength dispersion at the UATRS division of the National Center for Scientific Research. Moreover, the XRD was used to investigate the changes in the mineralogical composition. It was obtained from Bruker Co. model D8 (The techniques employed in this study encompass reflectometry, high-resolution diffraction, in-plane grazing incidence diffraction (IP-GID), small-angle X-ray scattering (SAXS), as well as examinations into residual stress and texture).

Furthermore, a scanning electron microscope equipped with energy dispersive spectroscopy (SEM–EDX) was used to characterize the morphologies of the prepared PAB before and after adsorption; it was obtained from Philips XL 30. The operating conditions were low vacuum and 30 kV. BET analyzer type Nova Touch LX2, made by Quanta Chrome Company in the USA, was used to quantify the surface area, pore size, and pore volume before and after adsorption. The measurements were done using the standard volumetric method of nitrogen adsorption at 77 K. Utilizing a Perkin-Elmer 1720-x spectrometer, the functional groups of the *Phragmites australis* Biochar were identified using FTIR. The samples were compressed using a press with potassium bromide at a ratio of 1 mg product per 100 mg KBr, and the spectra were analyzed at a resolution of 2.00 cm^{-1} in the range of 4000–400 cm^{-1} .

Materials characterization

A Life Cycle Assessment (LCA) was conducted to evaluate the environmental impacts associated with the treatment of UASB effluent and Arma wastewater using three different adsorbent materials: Activated Carbon, Chitosan, and *Phragmites australis* biochar. The LCA followed ISO 14040/14044 guidelines and was performed using SimaPro© software.

Results and discussion

Phragmites australis biochar characterization

The chemical elemental analysis of PAB is shown in Table 4. The major constituents are found in traces. As demonstrated in Fig. 5a–i, FTIR of PAB was used to determine which



Table 4 Chemical elemental analysis of *Phragmites australis* Biochar (FABC)

Constituents (wt. %)	FABC	Constituents (wt%)	FABC
Na ₂ O	—	P ₂ O ₅	1.44
MgO	1.41	Cl	2.81
Al ₂ O ₃	4.32	K ₂ O	5.86
SiO ₂	21.40	CaO	1.52
Fe ₂ O ₃ (total)	0.826	Sr	0.0123
SO ₃	2.19	Br	0.00
Zn	0.0674	L.O.I	58.10

functional groups were accountable for the adsorption of organic matter, namely organic load (COD). As can be seen, the spectra revealed the presence of absorption peaks in the range.

Adsorbents characterization

XRD characterization

The XRD patterns of *Phragmites australis* Biochar in both oiled and processed buffalo effluent and wastewater without contaminants are displayed in Fig. 2a, c. In the biochar pattern of *Phragmites australis*, the distinctive peaks showed a prominent sharp peak at $2\theta=28^\circ$, which agrees with the Bruker software database entry COD 01-076-3362 KCL. The distinctive peaks showed a prominent peak at $2\theta=30^\circ$. That conforms to the database of Bruker software COD 00-038-1024. TiSbS3 For the XRD pattern for buffalo wastewater using *Phragmites australis* Biochar after adsorption. Some new broad peaks are observed after adsorption according to the database of Bruker software COD 00-023-1814 Palladium- β -aminoethylamido (ethylenediamine) triphenyl antimonychloride iodide $C_{26}H_{45}Cl_{12}I_2N_8Pd_2Sb$ and Haigera-chite, syn $3KH_{14}(PO_4)_8 \cdot 4H_2O$.

However, there is a clear change in peak intensity following adsorption in buffalo wastewater, suggesting that this does, in fact, indicate modification (Fig. 2b). The XRD examination revealed the chemical composition of the adsorbent, which consisted primarily of crystalline cellulose, as well as the presence of elements including Cl, I, N, Pd, Sb, and PO_4 groups. Crystallinity is a property of biomass that is affected by its molecular structure and can vary from plant to plant based on factors including lignin, cellulose, and hemicellulose content. One thing that stands out about the adsorbent that was made is how highly crystalline it is. It also has little peaks in the areas below 20° , meaning it is made of very amorphous species.

As shown in Fig. 2c After adsorption in oily wastewater using *Phragmites australis* biochar, some new broad peaks

are observed after adsorption according to the database of Bruker software COD 00-065-07987-(4-(4-(2,3-dichlorophenyl)piperazin-1-yl)butoxy)-3,4-dihydroquinolin-2(1H)-one hemipyridine, Abilify; Abilitat I Aripiprazole hemipyridine COD 00-040-1992 n-Nonacosane $C_{29}H_{60}$ and COD 00-054-1933 $C_{10}H_{26}N_4O_6V_2 \cdot 3H_2O$. In contrast, the intensity of peaks is highly changed, indicating that this does imply alteration after adsorption in oily wastewater Fig. 2c. XDR analysis provided the fingerprint of the crystalline solids in the adsorbent, mainly crystalline cellulose, and took some organic derivatives such as chlorophenyl, piperazine, quinoline, pyridine, and piprazole. Removing nano compounds and vanadium compounds is a very strong adsorbent because the crystallinity degree depends on the molecular arrangement of biomass and may vary mainly by the enrichment of the lignin, cellulose, and hemicellulose exchange sites from each plant. Notably, the produced adsorbent has a high degree of crystallinity and small peaks in the regions below 20° , representing highly amorphous species.

Figure 2d–f shows the XRD spectra of selected activated carbons. The broad fuzzy peaks C indicate that the carbon has mainly an amorphous structure. As shown in Fig. 2e, in buffalo wastewater after adsorption using AC as adsorbent, there are COD 00-053-1627 at 2θ 5 $C_{164}H_{298}N_4O_3$, and COD 00-065-1436 at 2θ 8 $C_{93}H_{175}N_2O_{22}P$ refer to the adsorption of elements such as phosphorus and nitrogen. As shown in Fig. 2f in oily wastewater after adsorption using AC as adsorbent, there are COD 00-029-0084 at 2θ 24 Aluminum Silicate $AlSi_{0.5}O_{2.5}$, and COD 00-044-1058 at 2θ 22&42 Cobalt Germanium Co_2Ge refer to the adsorption of elements such as cobalt, germanium, and aluminum. The characteristic peaks of chitosan (CS) exhibited a major broad peak at $2\theta=19^\circ$ that conformed to the Bruker software COD 7114110, 7150157, 8100678 database. As shown in Fig. 2h, the characteristic peaks of buffalo waste water using chitosan (CS) after adsorption exhibited a major broad peak at $2\theta=16^\circ$ that conformed to the database of Bruker software COD 00-070-1335 poly(1,1,2,2-tetrafluorobutane-1,4-diyl); poly(ethene-co tetrafluoroethene); Tefzel I Ethylene tetrafluoroethylene ($C_4H_4F_4$)_n, COD0 00-062-1711 Poly(styrene-acrylic acid) ($CH_2CH(C_6H_5)$)_n($CH_2CH(COOH)$)_n, COD00-057-1528 Poly(ethylene oxide) (CH_2CH_2O)_n only flour that removed.

As shown in Fig. 2i, the characterization peak of oily wastewater using chitosan after adsorption exhibited a major peak at COD 00-054-1987 Piper adenium nitrate $C_5H_{12}N_2O_3$, COD 00-043-1571 Ytterbium tris (triethylenediamine dioxide) triperchlorate trihydrate $C_{18}H_{36}N_6O_6 \cdot C_{13}O_{12}Yb \cdot 3H_2O$, COD00-004-0037 Diamyl sodium sulfosuccinate $C_{14}H_{25}NaO_7S$ and COD 00-057-1528 Poly(ethylene oxide)(CH_2CH_2O)_n.



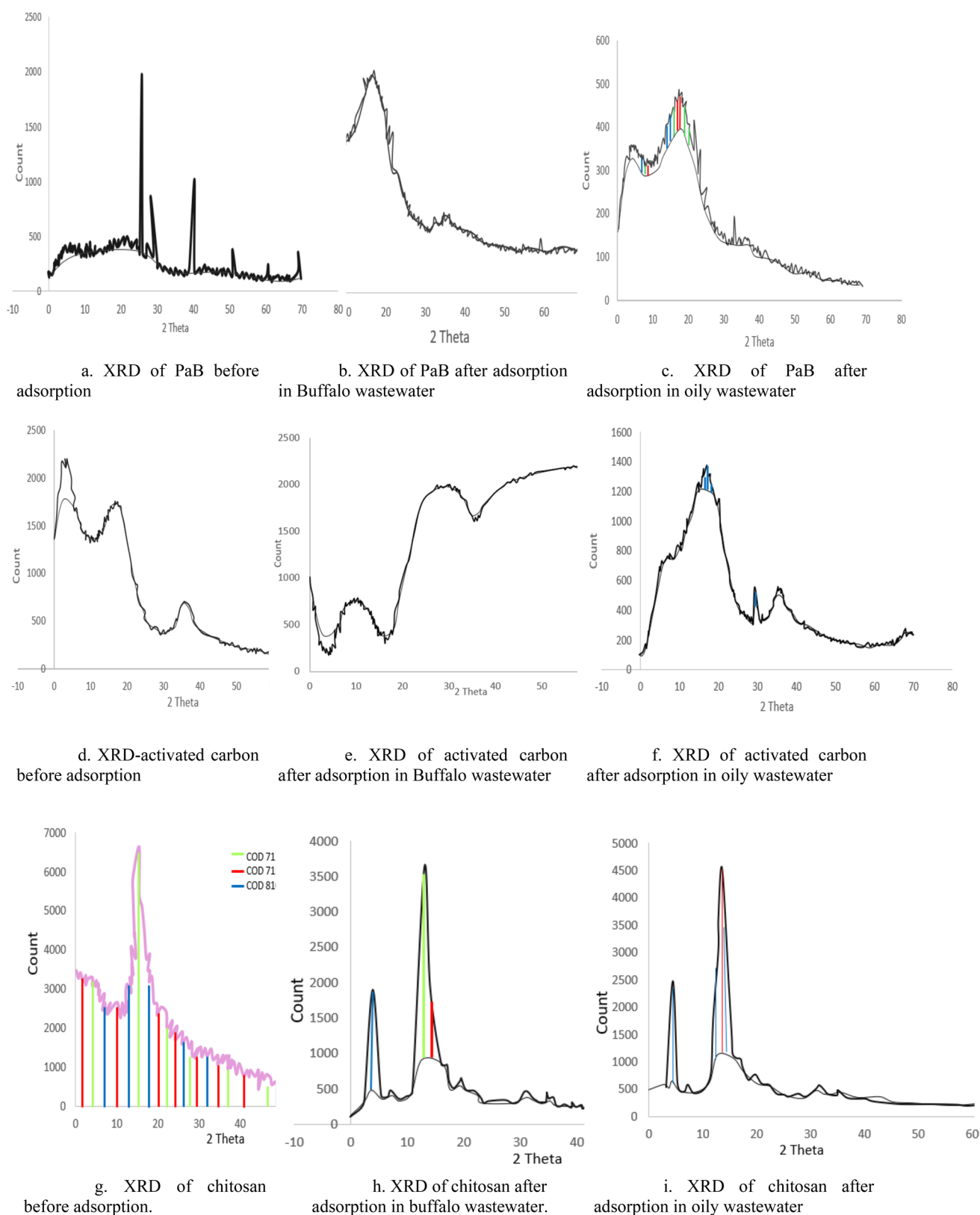
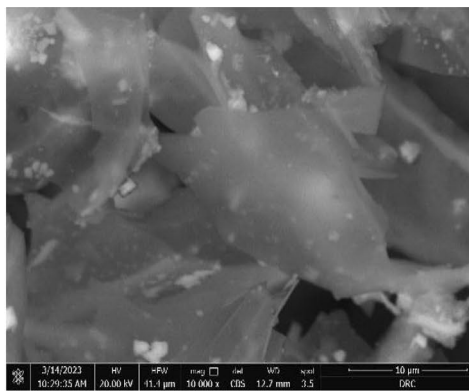


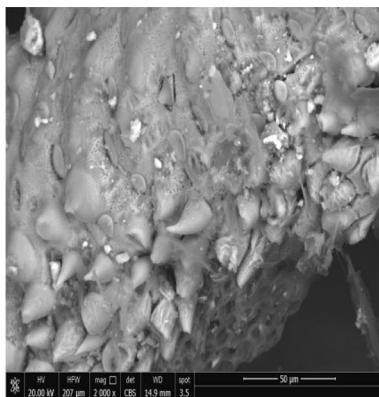
Fig. 2 a XRD of PaB before adsorption. b XRD of PaB after adsorption in Buffalo wastewater. c XRD of PaB after adsorption in oily wastewater. d XRD-activated carbon before adsorption. e XRD of activated carbon after adsorption in Buffalo wastewater. f XRD of

activated carbon after adsorption in oily wastewater. g XRD of chitosan before adsorption. h XRD of chitosan after adsorption in buffalo wastewater. i XRD of chitosan after adsorption in oily wastewater

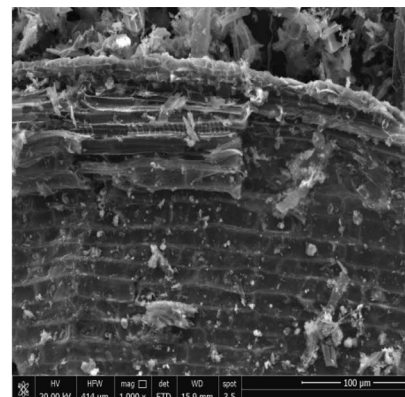




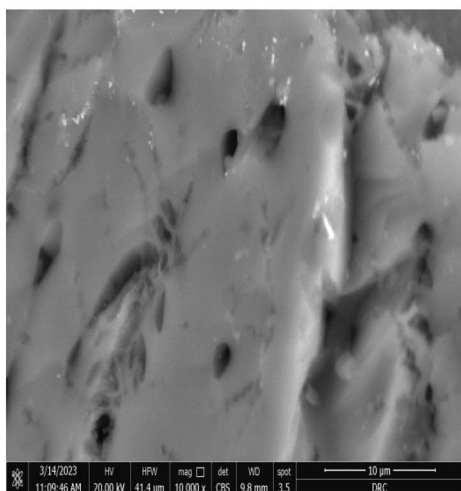
a. SEM of *Phragmites australis* biochar before adsorption



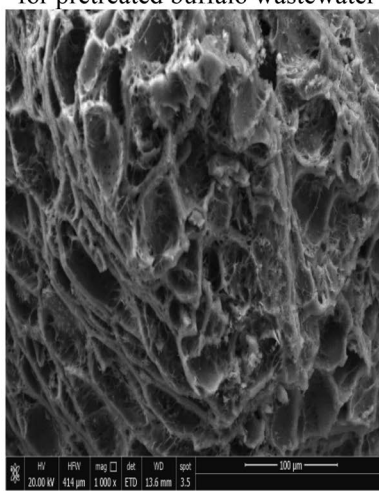
b. SEM of *Phragmites australis* biochar after adsorption for pretreated buffalo wastewater



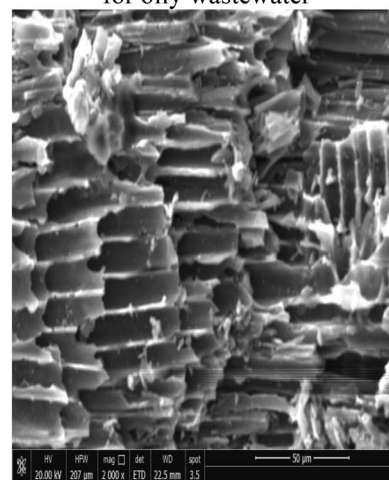
c. SEM of *Phragmites australis* biochar after adsorption for oily wastewater



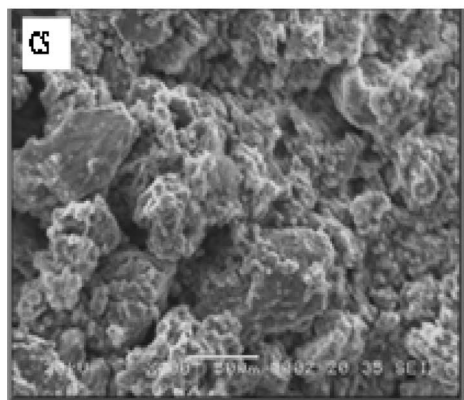
d. SEM-activated carbon before adsorption



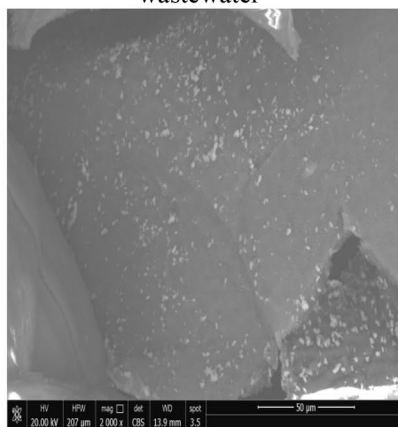
e. SEM of AC after adsorption for pretreated buffalo wastewater



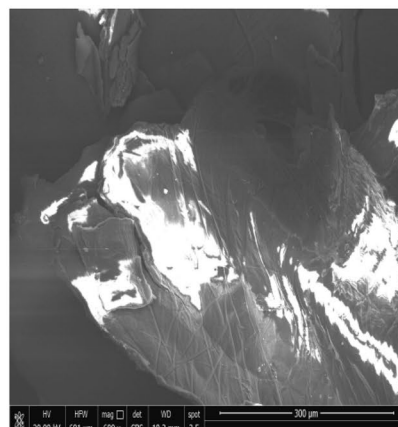
f. SEM of AC after adsorption for oily wastewater



g. SEM-chitosan before adsorption



h. SEM of chitosan after adsorption for pretreated buffalo wastewater



i. SEM of chitosan after adsorption for oily wastewater



Fig. 3 **a** SEM of *Phragmites australis* biochar before adsorption. **b** SEM of *Phragmites australis* biochar after adsorption for pretreated buffalo wastewater. **c** SEM of *Phragmites australis* biochar after adsorption for oily wastewater. **d** SEM-activated carbon before adsorption. **e**. SEM of AC after adsorption for pretreated buffalo wastewater. **f** SEM of AC after adsorption for oily wastewater. **g** SEM-chitosan before adsorption. **h** SEM of chitosan after adsorption for pretreated buffalo wastewater. **i** SEM of chitosan after adsorption for oily wastewater

Scanning Electron Microscopy (SEM)

The SEM is appropriate for investigating the change of surface and physical formations of adsorbents before and after organic and inorganic impurities adsorption, as shown in Fig. 3a. Before adsorption, the surface of *Phragmites australis* biochar smoothly formed several holes, as shown in Fig. 3b. After the absorption of impurities from buffalo wastewater, SEM images indicated that the surfaces are irregular and agglomerate particles with bigger interstitial holes, and the pores are filled; SEM results in Fig. 3c constructed of aggregates particles with bigger interstitial holes have developments of surfaces with several cavities due to collection and impregnation of some organic molecules and the pores are filled, the surface was irregular and agglomerate after adsorption. The SEM results reveal that these structures gave a more widespread surface area after adsorption.

The SEM result of activated carbon as an adsorbent Fig. 3d before adsorption has smoothly formed a few holes that indicate it is not as strong as the reed adsorbent. Figure 3e, after adsorption of buffalo wastewater using AC, manifested a definite shape, including small irregular bits with minute diameters that aren't related to each other, at Fig. 3f after adsorption of oily wastewater using AC the SEM photographs constructed of aggregates with bigger holes and developments of surface and the pores are filled with organic matters and the surface were irregular and agglomerate after adsorption.

The SEM result of chitosan as adsorbent Fig. 3g before adsorption has constructed of aggregates formed few holes that indicate it isn't stronger than reeds and AC adsorbent, at Fig. 3h after adsorption of buffalo wastewater using chitosan as adsorbent have manifested definite shape and smooth surface including small bits spread related to each other, at Fig. 3i after adsorption of oily wastewater using chitosan as adsorbent the SEM photographs constructed of smooth surface and reduction of surface after adsorption.

EDX

According to Fig. 4a, the EDX result of *Phragmites australis* biochar prior to adsorption indicates that it contains C & O & Cl Wt% 75.61 & 18.31 & 2.9, respectively. Figure 4b illustrates the adsorption process for pretreated buffalo

wastewater, which results in a C 55.2 reduction and an O 21.1 increase. Additionally, N, Al, Si, P, K, and Ca were identified. After adsorption in oily wastewater, C increased to 68.1 as an indication of the adsorption of organic compounds. There was no nitrogen, oxygen reduced to 7.9, Al, Si, phosphorus, and calcium were found, and K, S, and Cl were found.

For AC as an adsorbent, Fig. 4d shows that before adsorption, C has a very high peak and very small O, S, and Ca peaks. After adsorption in pretreated buffalo wastewater Fig. 4e, one change indicates less efficiency of the adsorption process using AC as an adsorbent. Still, in Fig. 4f with oily wastewater, C Wt% 91.8 reduced; there aren't S or K according to the adsorption of organic compounds.

In Fig. 4g, using chitosan before adsorption has a high concentration of C, N, and O. After adsorption for pretreated buffalo wastewater, Fig. 4h, C & N & O Wt% 38.5, 19.3, 40.3, respectively, there aren't P, K, and Ca 1.7%. In Fig. 4i, the result of oily wastewater slightly increased, indicating that a few organic compounds were removed.

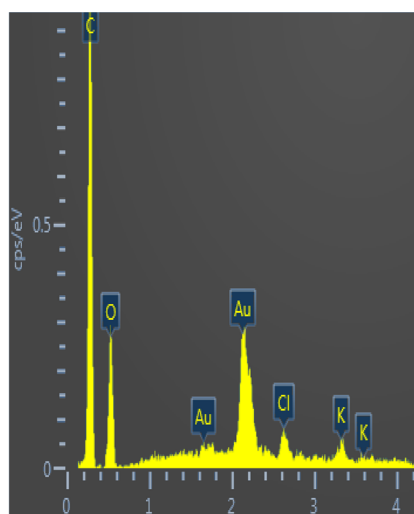
FTIR spectroscopy

Functional groups and corresponding FTIR peaks are summarized in Table 5. FTIR results show the interactions between the phenolic O–H bonds and unsaturated aliphatic structure for wastewater using *Phragmites australis* biochar adsorbent. When using activated carbon, there is no interaction with the O–H group after wastewater adsorption. Still, there is an organic compound at CH_2 out of the aromatic ring, and some heavy metals are removed. No significant differences exist between buffalo and oily wastewater results using chitosan after adsorption (Fig. 5).

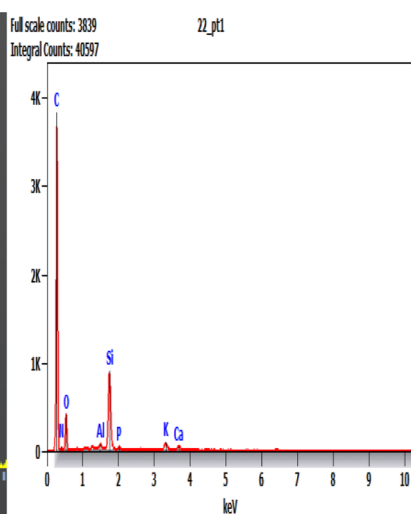
The Brunner–Emmett–Teller analyzer (BET)

The size, volume, and surface area of solid porous materials are all measured by BET. It provides crucial information on the physical structure of a material based on its adsorbent surface area, which impacts the solid's interaction with its surroundings. The adsorbent's surface area and pore size under study are evaluated using the nitrogen adsorption–desorption analyzer. The materials under study have their nitrogen adsorption–desorption isotherm curves shown in Fig. 6a. Adsorption of ions onto *Phragmites australis* biochar causes a discernible shift in the isotherms. Table 6 shows that the PAB has a specific surface area (SBET) of $3.22 \text{ m}^2/\text{g}$, a pore volume of 211.58 cc/g , and a pore size of 28.55 nm . On the contrary, after ion adsorption, the surface area ($6.354 \text{ m}^2/\text{g}$), pore volume (0.0377 cc/g), and pore size (23.78 nm) for pretreated buffalo wastewater it is almost the same for oily wastewater. The results are decreased because of pore-blocking with ions. The results showed that

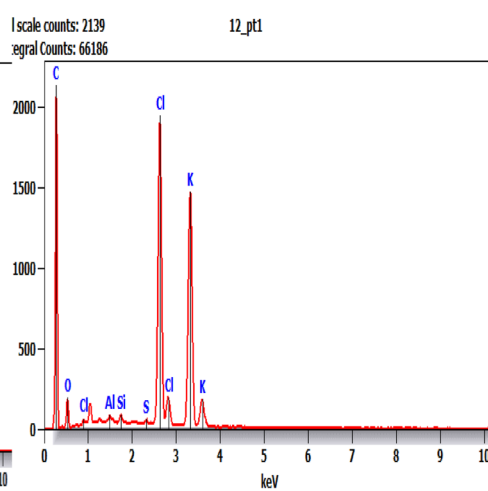




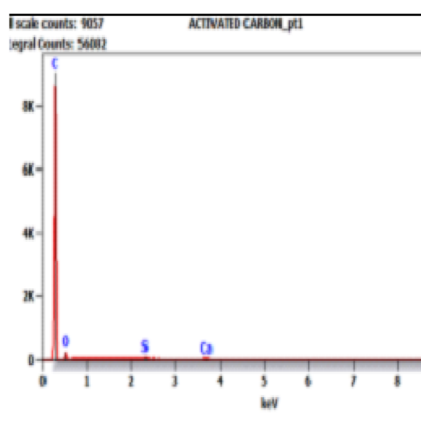
a. EDX of *Phragmites australis* biochar before adsorption.



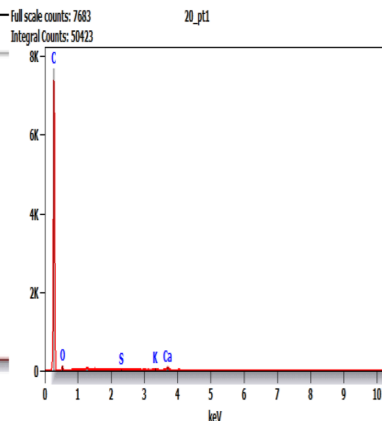
b. EDX of *Phragmites australis* biochar after adsorption for pretreated buffalo wastewater.



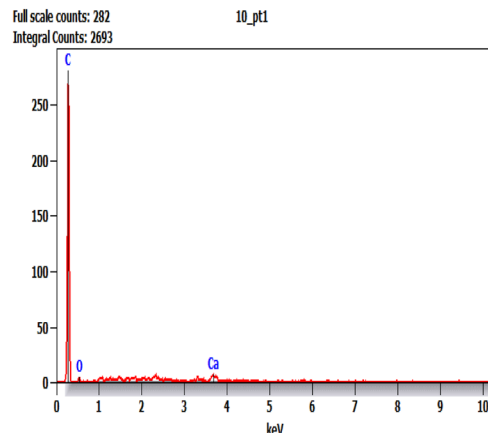
c. EDX of *Phragmites australis* biochar after adsorption for oily wastewater.



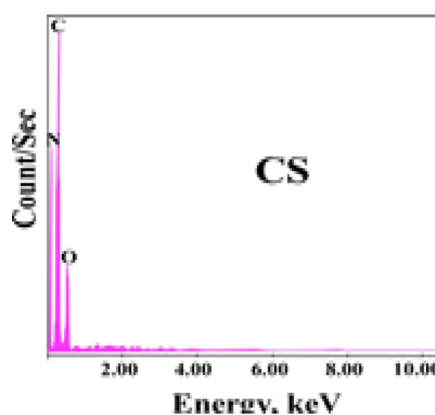
d. EDX of activated carbon before adsorption



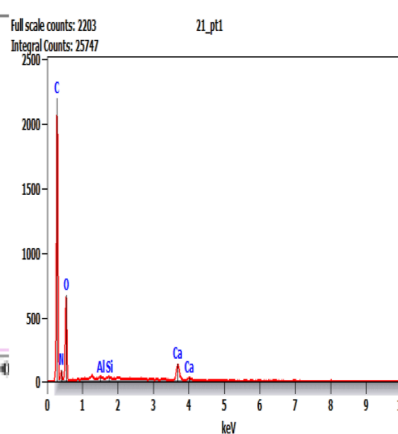
e. EDX of activated carbon after adsorption in pretreated buffalo wastewater



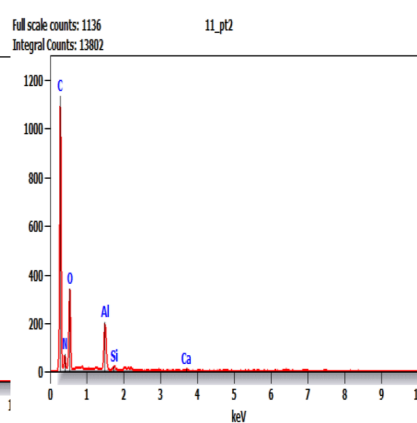
f. EDX of activated carbon after adsorption in oily wastewater



g. EDX of chitosan before adsorption.



h. EDX of chitosan after adsorption for pretreated buffalo wastewater



i. EDX of chitosan after adsorption for oily wastewater.



Fig. 4 **a** EDX of *Phragmites australis* biochar before adsorption. **b** EDX of *Phragmites australis* biochar after adsorption for pretreated buffalo wastewater. **c** EDX of *Phragmites australis* biochar after adsorption for oily wastewater. **d** EDX of activated carbon before adsorption. **e** EDX of activated carbon after adsorption in pretreated buffalo wastewater. **f** EDX of activated carbon after adsorption in oily wastewater. **g** EDX of chitosan before adsorption. **h** EDX of chitosan after adsorption for pretreated buffalo wastewater. **i** EDX of chitosan after adsorption for oily wastewater

phosphate ions, metals, and organic structures are powerfully absorbed by the *Phragmites australis* biochar, which has a negative surface charge and facilitates the adsorption of positively charged compounds in water and wastewater treatment (Mohamed et al. 2024).

Activated carbon after adsorption in oily wastewater has S_{bet} 466.85 high increase in surface area. Still, in pretreated buffalo wastewater, there aren't changes in pore size that are the same according to weak interaction in oily water only. As Table 6 shows, CS adsorption S_{bet} decreases according to the interaction after adsorption, and it is higher in oily water than in buffalo according to interaction with organic structure. Pore volume doubles in oily wastewater after adsorption and decreases in pretreated buffalo wastewater; pore size increases after adsorption.

ANOVA of COD removal

Table 7 presents the ANOVA results for COD removal, indicating that the model is highly significant. The F-value of 2.49 and p value of 0.133 (below the threshold of 0.25) suggest the model adequately explains COD removal variability, with an 87.57% confidence level, leaving approximately 12% of the variability unexplained. The normal probability plot of residuals (Fig. 7) confirms that the residuals are normally distributed, meeting ANOVA's assumptions and validating the model's robustness, consistent with findings by Koyuncu et al. (2025) in their study on heavy metal adsorption.

The analysis identifies wastewater type ($p=0.048$) as the most significant linear factor, contributing 12.75% to the variability in COD removal efficiency. The adsorbent material is also significant, with an 8.37% contribution ($p=0.213$). Among two-way interactions, “adsorbent material and contact time” has the strongest effect, contributing 6.86% with a p value of 0.079. The interaction between “wastewater type and contact time” contributes 4.48% ($p=0.127$), while “adsorbent material and wastewater type” contributes 9.97% ($p=0.171$), all indicating varying degrees of influence.

Three-way interactions also play a role: “adsorbent material, wastewater type, and contact time” contributes 8.38% ($p=0.063$), and “adsorbent material, wastewater type, and dose” adds 9.57% ($p=0.180$), demonstrating complex interdependencies. However, individual factors like contact time (1.24%) and dose (0.43%) have negligible effects, as their p

values exceed the 0.25 threshold. Overall, the results highlight the critical impact of wastewater type, adsorbent material, and specific interactions on COD removal efficiency.

The Pareto chart (Fig. 8) highlights significant factors in COD removal, with a critical value set at 1.214. Bars exceeding this threshold indicate important variables: A (Adsorbent Material), B (Wastewater Type), two-way interactions AC (Adsorbent Material $\times$ Contact Time) and BC (Wastewater Type $\times$ Contact Time), and three-way interactions ABC (Adsorbent Material $\times$ Wastewater Type $\times$ Contact Time) and ABD (Adsorbent Material $\times$ Wastewater Type $\times$ Dose).

These results underscore the crucial role of wastewater type and its interactions in COD removal. Similar findings by Wald et al. (2019) confirmed the significance of these interactions in their study on COD removal from textile wastewater.

The main effects plot for COD removal

Figure 9 illustrates the main effects on the COD Removal Rate (COD R.R.). Using UASB effluent (2) as the wastewater type yields the highest efficiency, around 90%, compared to oily wastewater (1) at approximately 83%. This improved performance is due to the lower initial COD (603 mg/L) and BOD (173.55 mg/L) of UASB effluent, making it easier to treat than oily wastewater with higher COD (1396.25 mg/L) and BOD (862.65 mg/L).

Phragmites australis biochar (2) demonstrates superior adsorbent performance, achieving about 89% efficiency compared to activated carbon and chitosan. Contact time negatively impacts efficiency, decreasing from 87% at 20 min to 84% at 90 min as active sites become less accessible and equilibrium conditions limit further adsorption. This trend aligns with findings by Gupta et al. (2024), Yadav and Indurkar (2021), who noted that prolonged contact does not always enhance efficiency.

The adsorbent dose has minimal influence, with efficiency ranging from 86% at 0.5 g/L to 87% at 6.5 g/L, suggesting equilibrium is reached early. Increasing the dose beyond saturation does not significantly enhance removal. Studies using *Phragmites australis* biochar reported similar high efficiencies, especially with UASB effluent, due to its reduced pollutant complexity compared to oily wastewater (Abedi and Mojiri 2019; Zhang et al. 2023).

The interaction plot for COD removal

The strength of the interaction increases as the number of nonparallel lines increases (Mathialagan and Viraraghavan 2005). It was clear from this interaction effect that the strength of the correlation between the parameters and COD removal varied with parameter levels (Fig. 10).



Table 5 FTIR spectrum value and functional groups

Frequency cm ⁻¹	Assignment Oily	Suggested peak Oily	Frequency cm ⁻¹ buf- falo	Assignment buffalo	Suggested peak Buffalo	Frequency- oilycm-1	Assignment oily	Suggested peak oily
3390.86	O–H	Alcohol	3839.9	O–H	Alcohol	3839.9	O–H	Alcohol
1732.08	C=O	Stretching vibrations	3753.54	O–H	Vibration cel- lulose	3752.54	O–H	Vibration cel- lulose
1635.64	O–H	Bending (of H ₂ O)	3088.02	C–H	Methyl cel- lulose	3135.99	C–H	Methyl cel- lulose
1371.39	O–H	Bending	2699.51	C–H ₂ O	Hemi cel- lulose	2661.71	C–H ₂ O	Hemi cellulose
1250.22	C–O	Stretching	2257.75	N=C=O	Isocyanate	2345.97	O=C=O	Carbon dioxide
1161.15	C–OH	Bending	2091.95	C=C=C	Allene	2095	C=C=C	Allene
1103.28	C–O–H	(OH associa- tion)	1831	C=O	Streching vibration	1839.21	C=O	Streching vibra- tion
1060.85	C–OH	Bending	1649.7	O–H	Bending H ₂ O	1652.40	O–H	Bending H ₂ O
1045.42	C–O–C	Stretching (pyranose ring skel- etal)	1529.15	C–O		1484.71	C–O	
			1376.8	O–H	Carboxylate	1087.20		
			904.65	C–H	Degradation	976.74	C–H	Degradation
			763.19	C=C	Angular deformation	741.98	C=C	Angular defor- mation
			706.46	C–O–C	Ethere	691.04	C–O–C	Ethere
						625.84		
3422	O–H	Hydroxyl group	3829	O–H	Alcoholic	3748.53	O–H	Alcoholic
2824	C=C	Unsaturated	3736	O–H	Vibration	3090	C–H	Methyl
2346	C–H	Strong elec- tronegative	3066	C–H	Methyl Out plane	2416.94	C–H	Strong electron- egative
1622	Aromatic ring		2346	C–H	Strong elec- tronegative	1845	C=O	Stretching vibration
1444	O–H	Bending	1834	C=O	Stretching	1081	CH ₂	Aliphatic
1118	–C–H	Aliphatic	1716	C=C	Unsaturation	899.29	C–H	Angular degra- dation
874	C–H	Out of plane	1531	C–O		707.7	C–O–C	Ether
			1382	Cyclic	Ring	627.36		Heavy metal
			957	C–H	Degradation	514.08		Heavy metal
			809	C=C	Angular deformation			
			691	C–O–C	Ether			
			509		Heavy metal			
3550–3200	–OH –NH	Overlapping	3901.75	O–H	Alcoholic	3897.18	O–H	Alcoholic
2915–2865	–CH ₂		3756	–NH		3684	–NH	
1646	–NH		3555	Ring	Aromatic	3435	Ring	Aromatic
1550	C=N		2990.55	–CH ₂		3070	–CH ₂	
1434	–NH	Deformation	2741	C–H H ₂ O	Hemi	2555.63	–SH	Week thiol
1373	C–O	Vibration	2549	–SH	Week thiol	2393.02	O=C=O	Carbon dioxide
1311	C–O–C	Ether	2344	O=C=O	Carbon dioxide	2247.56	N=C=O	Isocyanate
1166	C–N	Stretching	2260	N=C=O	Isocyanate	2031.68	C=C=C	
1018	C–N	Stretching	2091	C=C=C	Allene	1938	C=C=C	Allene
894		D–glucose	1895	C=O	Anhydride	1867	C=O	Anhydride



Table 5 (continued)

Frequency cm ⁻¹	Assignment Oily	Suggested peak Oily	Frequency cm ⁻¹ buf- falo	Assignment buffalo	Suggested peak Buffalo	Frequency- oilycm-1	Assignment oily	Suggested peak oily
			1523	C=N		1709	C=N	
			1379	N-H	Deformation	1473	N-H	Deformation
			1279	C-O-C	Ether	1284	C-O-C	Ether
			1057	C-N		996.75	C-N	Stretching
			982	C-N	Stretching	767.56	C=C	Angular
			892	Si-OH		513.31		Heavy metal
			769	C=C	Angular			
			703	C-O-C	Stretching			
			612	PO ₄				
			516		Heavy metal			

Interaction between adsorbent material and contact time

The interaction between adsorbent material and contact time significantly influences COD removal efficiency. Figure 10 illustrates that *Phragmites australis* biochar achieves the most notable improvement, with COD removal rising from 84% at 20 min to 98% at 90 min, a 14% increase. This enhanced performance is attributed to biochar's increased surface area (from 3.22 to 6.354 m²/g) and reduced pore volume (from 211.58 to 0.0377 cc/g) after adsorption, indicating better contaminant penetration and site availability. The biochar's crystallinity, confirmed by XRD peaks at 2θ=28° and 30°, contributes to its superior adsorption capacity.

Conversely, activated carbon and chitosan show reduced efficiency with extended contact time. Activated carbon's COD removal decreases from 87 to 79%, an 8% drop, due to surface area reduction (from 316.47 to 311.22 m²/g) and pore blockage, as evidenced by broad XRD peaks indicating an amorphous structure. Similarly, chitosan's efficiency declines from 84 to 81%, a 3% decrease, alongside a reduction in surface area and limited adsorption capability due to its semi-crystalline structure, noted by a broad XRD peak at 2θ=19°. Gupta et al. (2024) reported similar trends, with activated carbon's efficiency dropping from 86 to 77% over 90 min due to pore saturation. Chitosan exhibited only minor fluctuations in performance, underscoring the challenges of maintaining high efficiency over extended contact times.

Interaction between wastewater type and contact time

The interaction between wastewater type and contact time influences COD removal efficiency. Figure 10 shows that for Oily Wastewater (Type 1), increasing contact time from 20 to 90 min results in a marginal 2% improvement in COD removal efficiency, from 82 to 84%. This limited increase is attributed to the high viscosity of the wastewater, which impedes mass transfer and slows adsorption kinetics. The

complex mixture of organic pollutants, characterized by high initial COD (1396.25 mg/L), BOD (862.65 mg/L), TDS (1408 mg/L), turbidity (605.9 NTU), and color (1730), further complicates effective adsorption.

Conversely, for UASB effluent (Type 2), COD removal efficiency decreases from 90 to 85% with extended contact time, a 5% reduction. This decline occurs because UASB effluent's simpler contaminant profile and lower initial COD (603 mg/L) allow for rapid adsorption initially, but the saturation of adsorption sites and equilibrium effects lead to reduced efficiency over time. Similar findings by Jaiswal et al. (2021) noted only slight improvements in oily wastewater COD removal due to high viscosity, while (Dai et al. 2019) observed efficient initial COD removal for simpler effluents, with effectiveness diminishing as equilibrium was approached.

Interaction between adsorbent material and wastewater type

The interaction between adsorbent material and wastewater type demonstrates that *Phragmites australis* biochar is notably more effective in COD removal compared to activated carbon and chitosan, especially for UASB effluent and oily wastewater. Figure 10 shows that biochar achieves a 10% increase in COD removal efficiency, from 82% for oily wastewater to 92% for UASB effluent. This improvement is due to biochar's high surface area (6.354 m²/g) and diverse functional groups, such as O-H and C=O, which allow it to maintain effectiveness across pH variations, efficiently adsorbing pollutants under neutral and slightly alkaline conditions.

On the other hand, activated carbon shows a slight decrease in efficiency, from 83% with oily wastewater to 81% for UASB effluent. Despite its high initial surface area, activated carbon's sensitivity to pH changes reduces active site availability and adsorption efficiency at higher



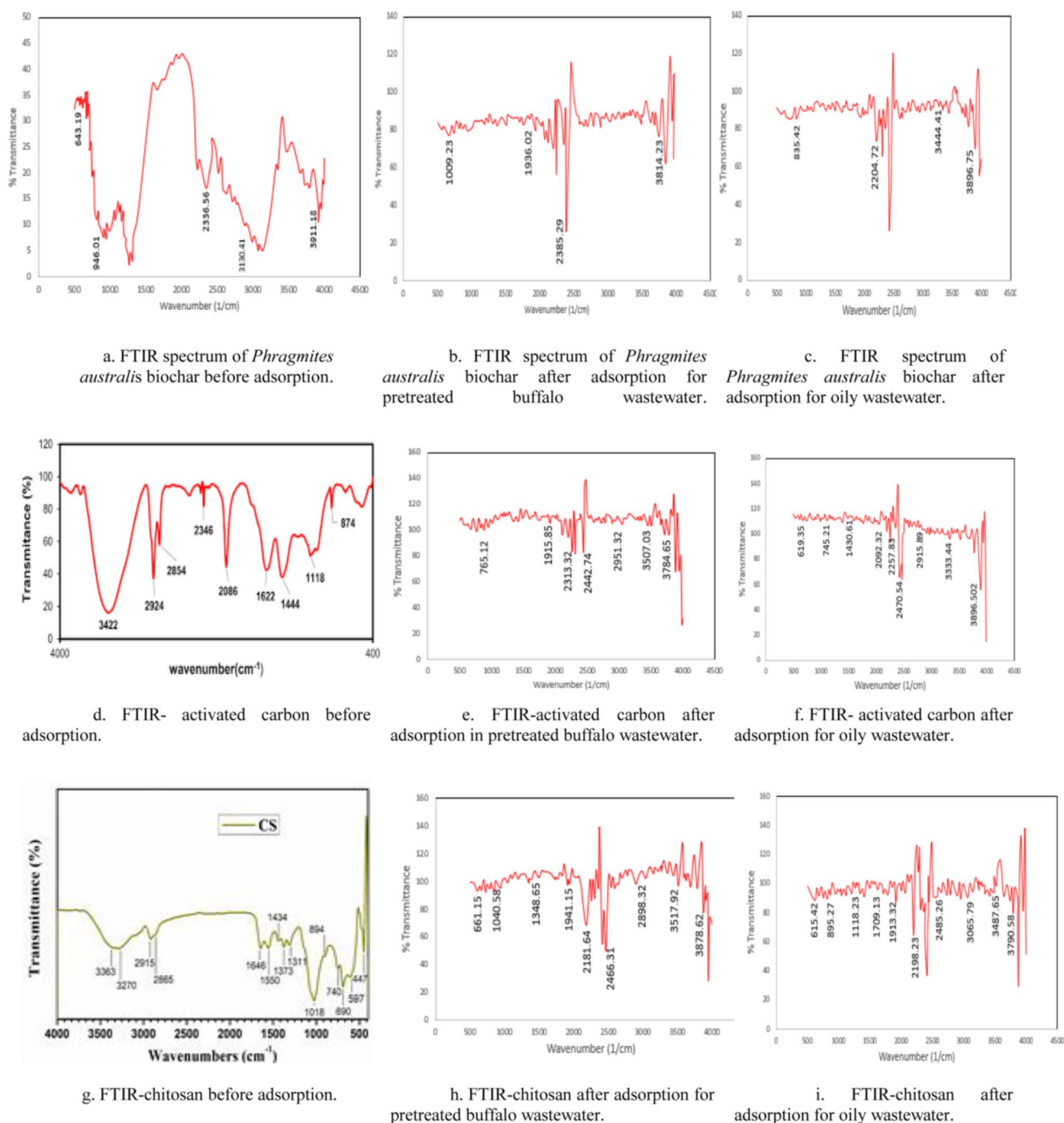


Fig. 5 **a** FTIR spectrum of *Phragmites australis* biochar before adsorption. **b** FTIR spectrum of *Phragmites australis* biochar after adsorption for pretreated buffalo wastewater. **c** FTIR spectrum of *Phragmites australis* biochar after adsorption for oily wastewater. **d** FTIR- activated carbon before adsorption. **e** FTIR-activated carbon

after adsorption in pretreated buffalo wastewater. **f** FTIR- activated carbon after adsorption for oily wastewater. **g** FTIR-chitosan before adsorption. **h** FTIR-chitosan after adsorption for pretreated buffalo wastewater. **i** FTIR-chitosan after adsorption for oily wastewater

pH levels. Chitosan displays a COD removal rate of 78% for oily wastewater and improves to 90% for UASB effluent. This variance is due to chitosan's reduced affinity for non-polar, hydrophobic compounds present in oily wastewater and its decreased efficiency in alkaline conditions,

where it loses its positive charge. In contrast, UASB effluent's simpler and more polar organic compounds facilitate more effective adsorption. Collivignarelli et al. (2021) found that biochar derived from agricultural waste improves COD removal efficiency by 15% for UASB effluent compared to



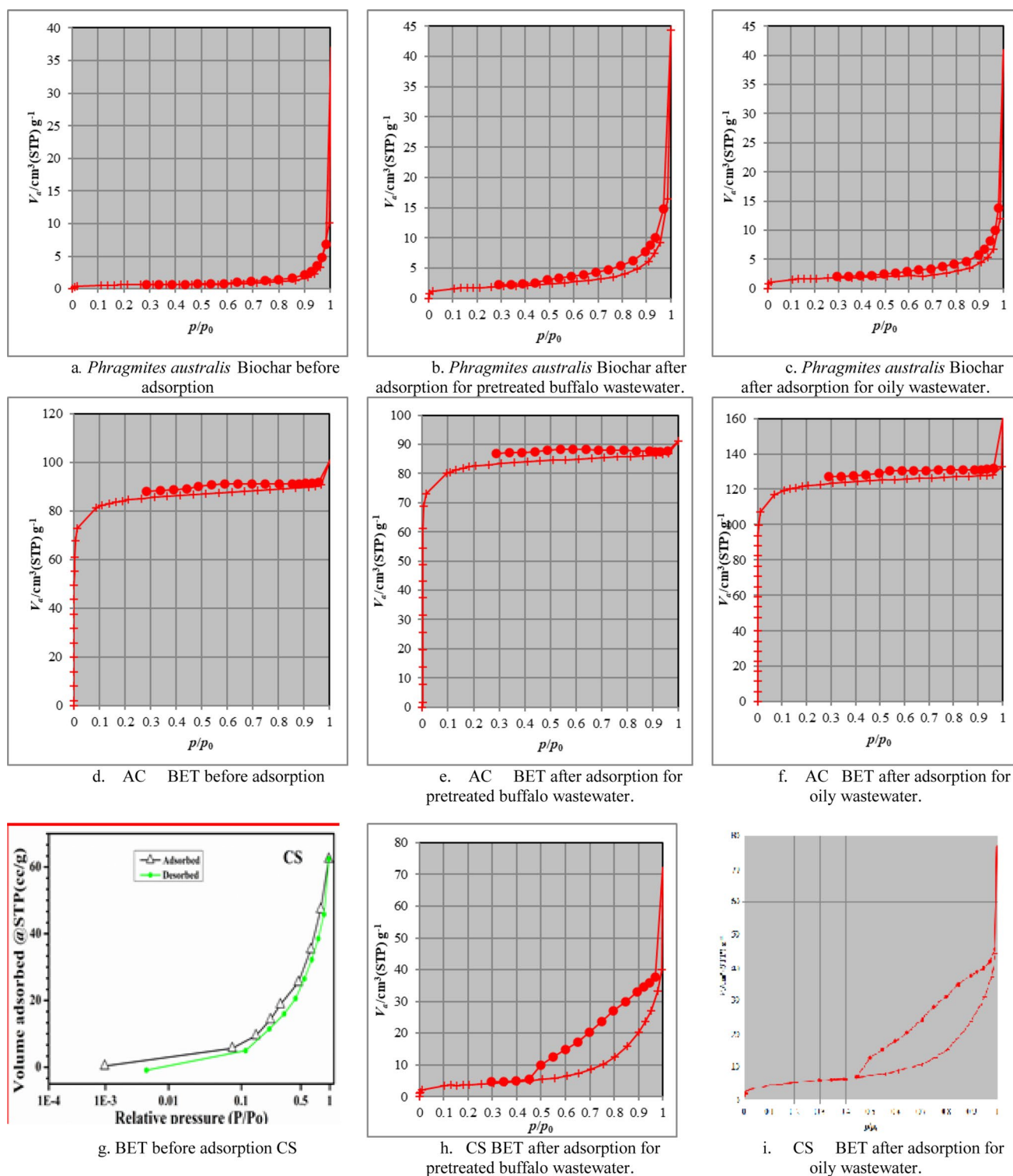


Fig. 6 **a** *Phragmites australis* Biochar before adsorption. **b** *Phragmites australis* Biochar after adsorption for pretreated buffalo wastewater. **c** *Phragmites australis* Biochar after adsorption for oily wastewater. **d** AC BET before adsorption. **e** AC BET after adsorption for

pretreated buffalo wastewater. **f** AC BET after adsorption for oily wastewater. **g** BET before adsorption CS. **h** CS BET after adsorption for pretreated buffalo wastewater. **i** CS BET after adsorption for oily wastewater



Table 6 The surface area (S_{BET}), the pore volume, and the pore size of *adsorbents* before and after adsorption for pretreated buffalo and oily wastewater

	Before adsorption	After adsorption for pre-treated buffalo wastewater	After adsorption for oily wastewater
Surface area S_{BET} , m^2/g <i>Phragmites</i>	3.22	6.354	6.19
Pore volume, cc/g <i>Phragmites</i>	211.58	0.0377	0.0332
Pore size, nm <i>Phragmites</i>	28.55	23.78	21.454
Surface area S_{BET} , m^2/g AC	316.47	311.22	466.85
Pore volume, cc/g AC	0.1508	0.1391	0.2039
Pore size, nm AC	1.9063	1.7877	1.747
Surface area S_{BET} , m^2/g CS	19.77	15.233	17.002
Pore volume, cc/g CS	0.033	0.03269	0.0657
Pore size, nm CS	2.65	17.341	15.448

Table 7 Analysis of variance (ANOVA) for COD removal ratio

Source	DF	Seq SS	Contribution (%)	Adj SS	Adj MS	F-Value	P value
Model	17	1545.53	87.57	1545.53	90.913	2.49	0.133
Linear	5	395.15	22.39	395.15	79.031	2.16	0.188
Adsorb. Material	2	147.71	8.37	147.71	73.855	2.02	0.213
WW Type	1	225.02	12.75	225.02	225.02	6.15	0.048
Contact time	1	21.94	1.24	21.94	21.938	0.60	0.468
Dose	1	0.48	0.03	0.48	0.485	0.01	0.912
2-Way Interactions	8	649.5	36.8	649.50	81.187	2.22	0.173
Adsorb.material*ww type	2	175.99	9.97	175.99	87.997	2.41	0.171
Adsor.material*contact time	2	292.59	16.58	292.59	146.296	4.00	0.079
Adsor.material*Dose	2	42.74	2.42	42.74	21.37	0.58	0.586
WW.Type*contact time	1	114.42	6.48	114.42	114.42	3.13	0.127
WW.Type*Dose	1	23.75	1.35	23.75	23.753	0.65	0.451
3-way interactions	4	500.88	28.38	500.88	125.219	3.42	0.087
Adsorb.material*WW.Type*contact time	2	331.93	18.81	331.93	165.965	4.54	0.063
Adsob.material*WW.Type*Dose	2	168.95	9.57	168.95	84.473	2.31	0.180
Error	6	219.36	12.43	219.36	36.560		
Total	23	231,764.89	100				

oily wastewater, thanks to its high porosity and stable surface functionality across different pH levels. Koyuncu et al. (2025) observed that activated carbon provides consistent but lower COD removal rates, with only a 2% efficiency variation across different wastewater types. Similarly, Singh et al. (2024) highlighted chitosan's superior performance with simpler effluents, achieving up to 88% COD removal for UASB effluent.

Numerical optimization for COD removal

The numerical optimization of COD removal is carried out using the desirability function method, which aims to find the optimal settings for maximum COD removal. In Fig. 11, the desirability function is used to optimize the process, with the objective being to achieve the highest

possible COD removal percentage. The results indicate that the maximum COD removal (97.75%) was achieved under the following optimal conditions: The Biochar dose (6.5 g/L) of *phragmites*, agitation speed 250 rpm, the wastewater type for buffalo wastewater of the Up-Flow Anaerobic Sludge Blanket effluent (2), and contact time 90 min. The combination of parameters that best achieves the intended response. In this case, the highest COD elimination (optimal $D = 0.9428$) is more successful when the desirability value is closer to 1. Similar optimization methods have shown that maximum COD removal (92.70%) for buffalo wastewater can be achieved at an optimal *Phragmites australis* biochar dose of 20 g/L, pH of 7.5, and type of bacteria (*Streptomyces hydrogenans* S11) (Mohamed et al. 2024a; b).



Fig. 7 Normal probability plot of standardized residual on the removal of COD

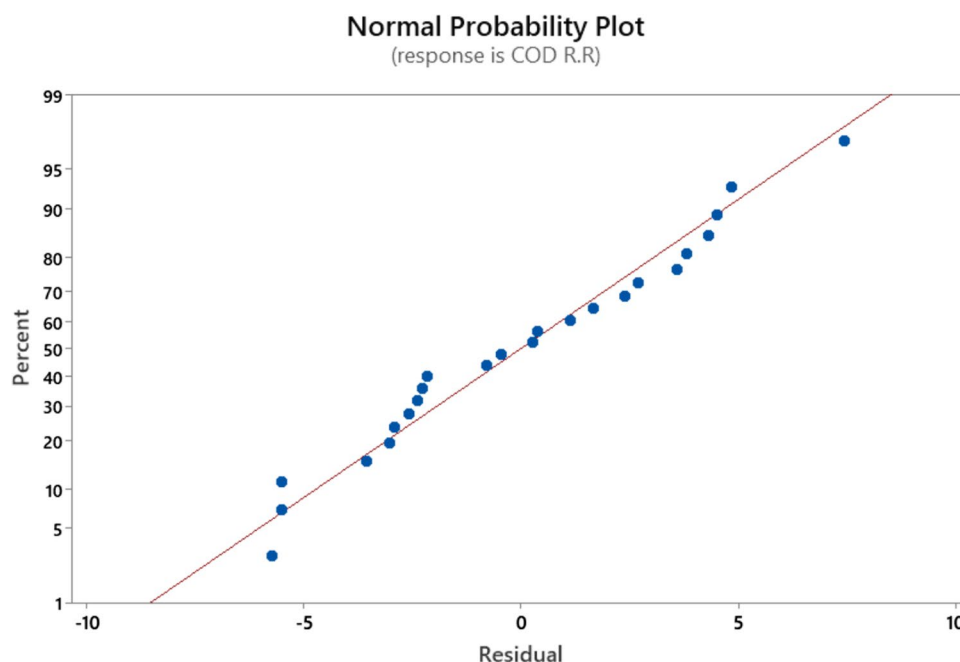
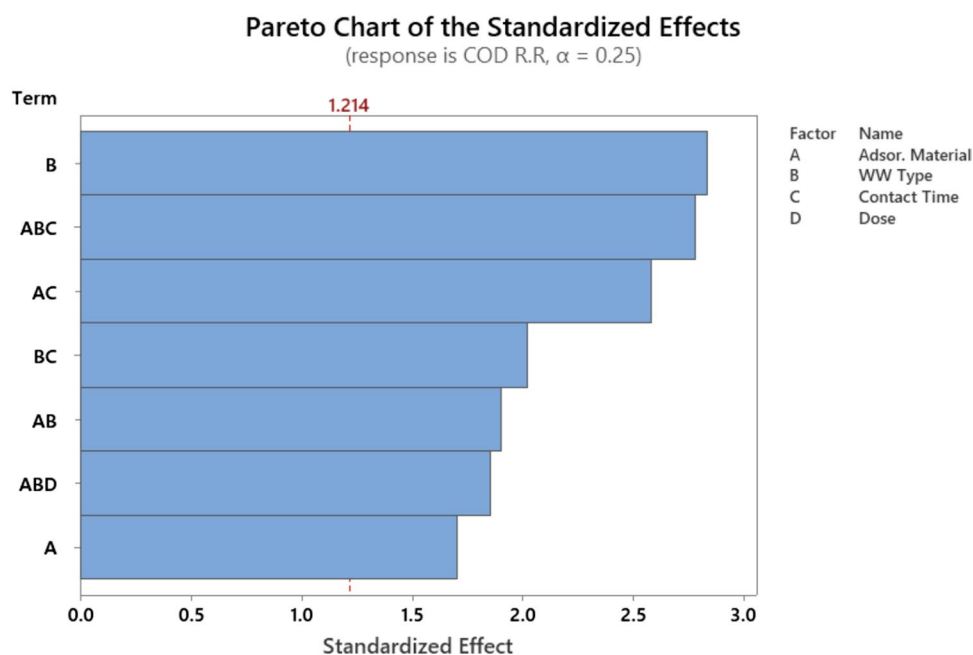


Fig. 8 Pareto chart of statistical effects on the removal of COD at $\alpha = 0.25$



ANOVA of phenol removal

The ANOVA for phenol removal confirms a highly significant model with an F-value of 84.34 and a p value of 0.012, well below the 0.25 threshold, ensuring strong alignment with experimental data at an 87.57% confidence level. Table 8 reveals that several factors and interactions significantly influence phenol removal efficiency. Among linear factors, adsorbent material ($p=0.010$) contributes 11.16%, wastewater type ($p=0.002$) contributes 27.51%, and

adsorbent material dose ($p=0.005$) contributes 21.46%, all indicating high significance. Contact time contributes marginally at 0.80% ($p=0.064$).

In two-way interactions, adsorbent material $\times$ dose ($p=0.005$) is highly influential, contributing 21.46%. Marginal effects are seen for contact time $\times$ wastewater type (0.99%, $p=0.052$), adsorbent material $\times$ wastewater type (1.61%, $p=0.066$), and adsorbent material $\times$ contact time (0.74%, $p=0.108$). Three-way interactions, particularly wastewater type $\times$ contact time $\times$ dose (6.31%,



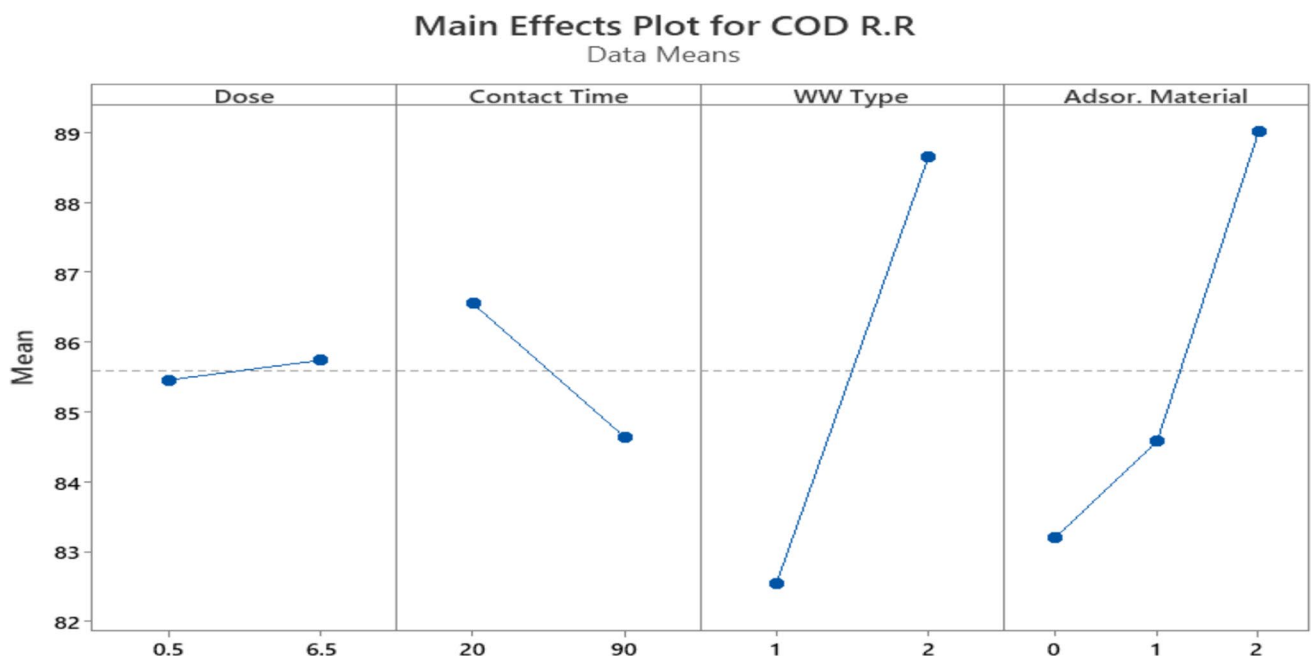


Fig. 9 The main effects plot for different parameters of COD Removal

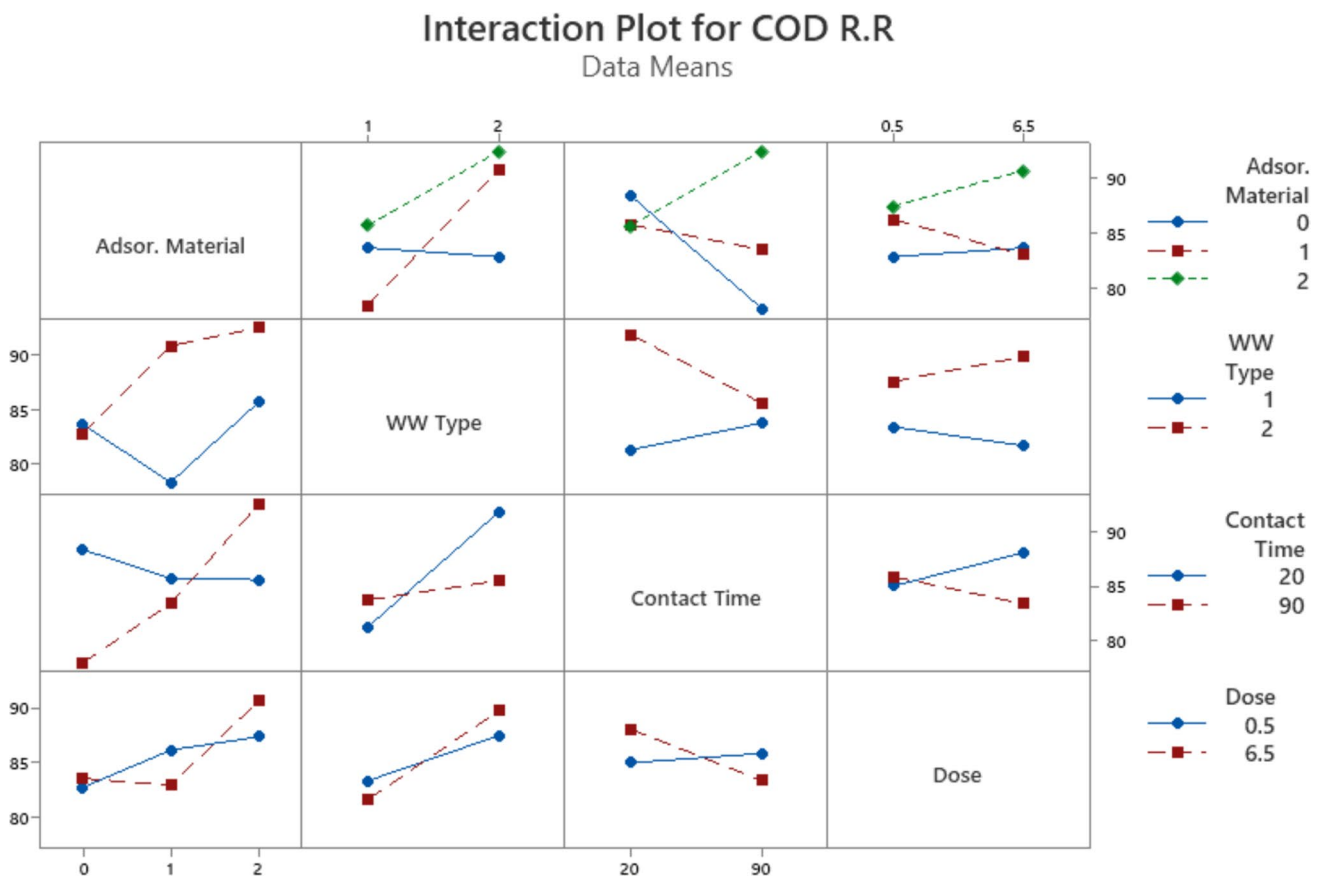
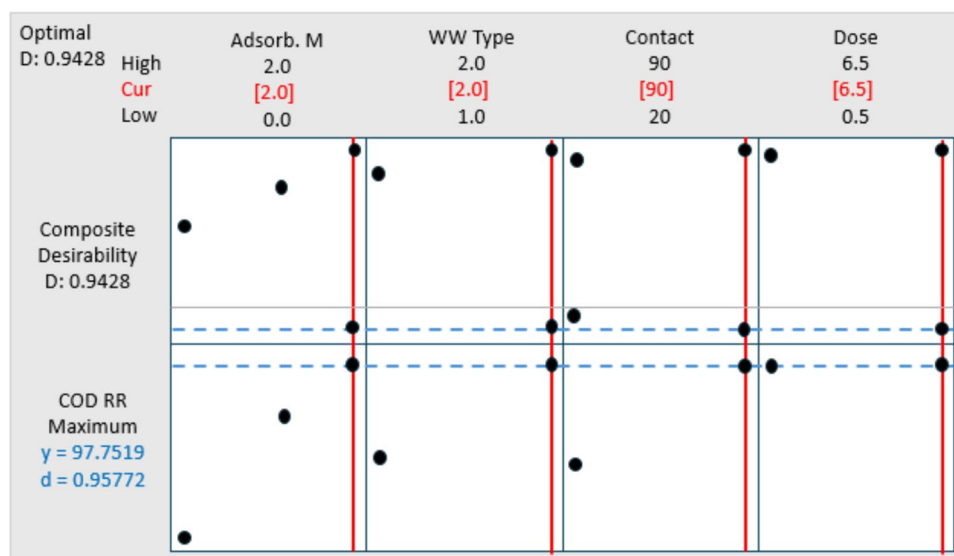


Fig. 10 Interaction plot for different parameters of COD Removal



Fig. 11 Desirability functions for the optimization of COD removal**Table 8** Analysis of variance (ANOVA) for phenol removal ratio

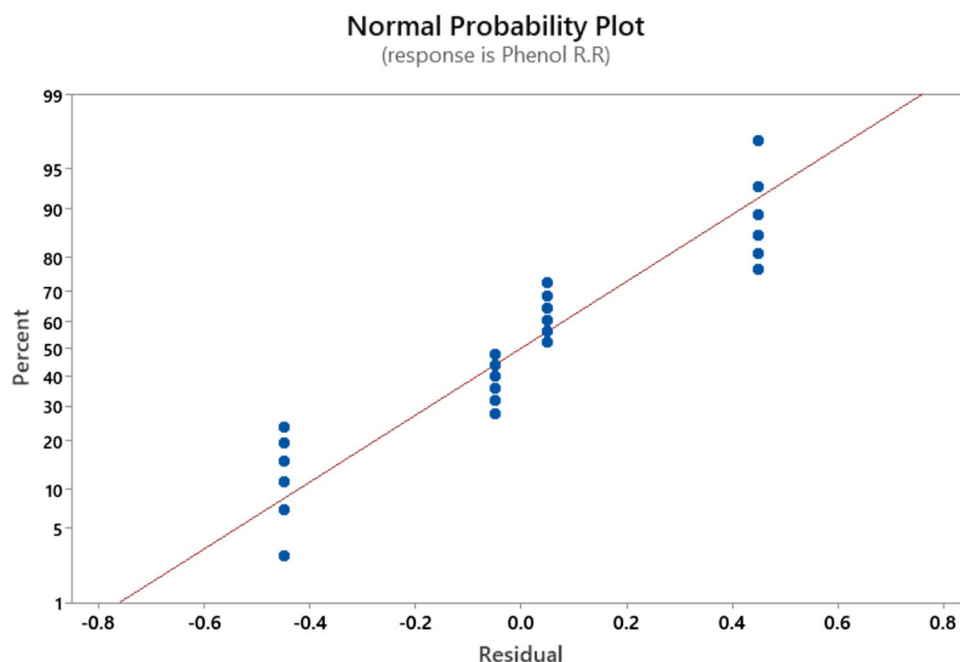
Source	DF	Seq SS	Contribution (%)	Adj SS	Adj MS	F-Value	P value
Model	21	2169.73	99.89	2169.73	103.321	84.34	0.012
Linear	5	1094.46	50.39	1094.46	218.892	178.67	0.006
Adsor. Material	2	242.39	11.16	242.39	121.195	98.93	0.010
WW Type	1	597.61	27.51	597.61	597.607	487.80	0.002
Contact Time	1	17.27	0.80	17.27	17.271	14.10	0.064
Dose	1	237.19	10.92	237.19	237.190	193.61	0.005
2-Way Interactions	7	542.81	24.99	542.81	77.544	63.30	0.016
Adsor. Material*WW Type	2	34.90	1.61	34.90	17.450	14.24	0.066
Adsor. Material*Contact Time	2	20.20	0.93	20.20	10.100	8.24	0.108
Adsor. Material*Dose	2	466.13	21.46	466.13	233.067	190.24	0.005
WW Type*Contact Time	1	21.57	0.99	21.57	21.574	17.61	0.052
3-Way Interactions	7	439.60	20.24	439.60	62.800	51.26	0.019
Adsor. Material*WW Type*Contact Time	2	137.09	6.31	137.09	68.546	55.95	0.018
Adsor. Material*WW Type*Dose	2	103.74	4.78	103.74	51.872	42.34	0.023
Adsor. Material*Contact Time*Dose	2	61.08	2.81	61.08	30.538	24.93	0.039
WW Type*Contact Time*Dose	1	137.69	6.34	137.69	137.689	112.39	0.009
4-Way Interactions	2	92.87	4.28	92.87	46.434	37.90	0.026
Adsor. Material*WW Type*Contact Time*Dose	2	92.87	4.28	92.87	46.434	37.90	0.026
Error	2	2.45	0.11	2.45	1.225		
Total	23	2172.18	100.00	2172.18			

$p = 0.009$), are highly significant, emphasizing the importance of combined effects. Other notable interactions include adsorbent material $\times$ wastewater type $\times$ contact time (4.61%, $p = 0.018$) and adsorbent material $\times$ wastewater type $\times$ dose (4.78%, $p = 0.023$). The adsorbent material $\times$ contact time $\times$ dose interaction (2.81%, $p = 0.039$) and the four-way interaction involving all factors (4.28%, $p = 0.026$) further highlight the complex dependencies in phenol removal.

The normal probability plot of residuals (Fig. 12) confirms model validity, with residuals aligning along the reference line, indicating no significant deviations from normality. This validates the model's predictive accuracy. Similar studies, such as (Ma et al. 2006) using rubber wood-derived activated carbon and Langmuir and Freundlich on phenolic adsorption onto biochar, also demonstrated robust models with normally distributed residuals, supporting the reliability of these findings.



Fig. 12 Normal probability plot of standardized residual on the removal of phenol



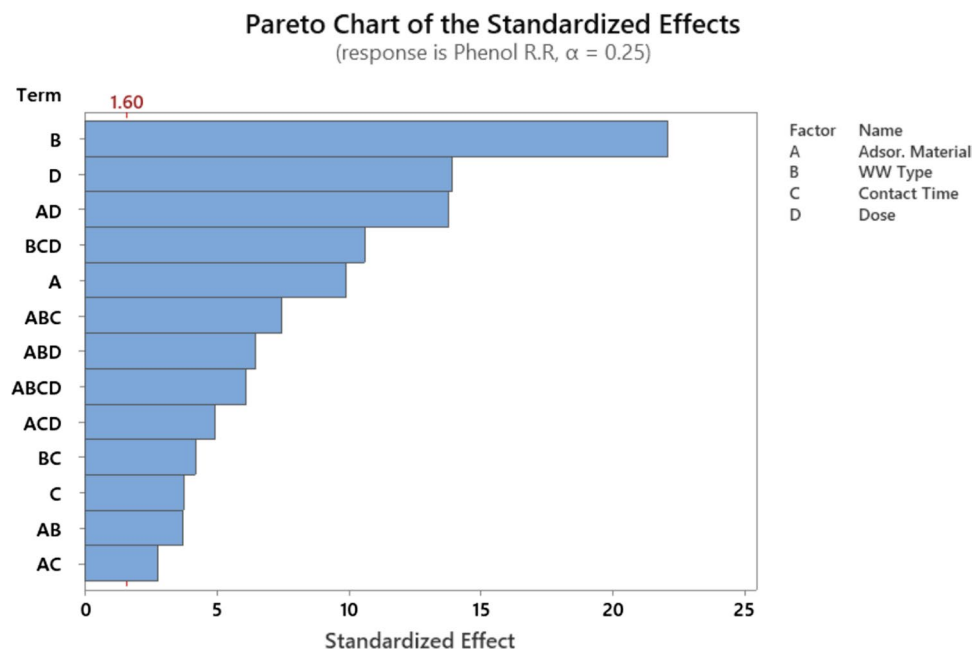
The Pareto chart (Fig. 13) illustrates the statistical significance of various parameters and interactions affecting phenol removal, with a critical value set at 1.60. Parameters with bars exceeding this threshold are deemed significant. Among the linear effects, wastewater type (B) is the most influential factor, followed by dose (D), adsorbent material (A), and contact time (C), with wastewater type having the greatest impact.

Significant two-way interactions include adsorbent material $\times$ dose (AD), wastewater type $\times$ contact time (BC),

adsorbent material $\times$ wastewater type (AB), and adsorbent material $\times$ contact time (AC). For three-way interactions, wastewater type $\times$ contact time $\times$ dose (BCD) is the most notable, followed by adsorbent material $\times$ wastewater type $\times$ contact time (ABC), adsorbent material $\times$ wastewater type $\times$ dose (ABD), and adsorbent material $\times$ contact time $\times$ dose (ACD). The four-way interaction involving all factors (ABCD) also crosses the critical threshold.

These findings emphasize the substantial impact of linear factors, particularly wastewater type (B), and complex

Fig. 13 Pareto chart of statistical effects on the removal of Phenol at $\alpha=0.25$



multi-factor interactions on phenol removal. Villegas et al. (2016) similarly found that adsorbent type and dosage significantly influence phenol removal efficiency in industrial wastewater treatment using activated carbon. Chaudhary et al. (2015) also reported the importance of adsorbent dosage and particle size when using fly ash for phenol removal, consistent with the interactions depicted in this analysis.

The main effect plots for phenol removal

Figure 14 highlights that wastewater type is the most significant factor affecting phenol removal efficiency. UASB effluent (Type 2) achieves over 72% removal, outperforming oily wastewater (Type 1) due to its lower pollutant complexity. *Phragmites australis* biochar (Type 2) is the most effective adsorbent, reaching 72% efficiency, thanks to its superior pore structure and functional groups. Increasing the adsorbent dose from 0.5 to 6.5 g/L improves efficiency from 65 to 72% as more adsorption sites become available. Contact time has a smaller impact, slightly increasing from 67 to 69% over 20 to 90 min, attributed to gradual site saturation. Similar trends have been confirmed by studies, such as those by Hameed (2009) and Chen et al. (2020), emphasizing the importance of adsorbent type and dose, with only minor gains from extended contact time.

The interaction plot for phenol removal

The results showed a significant interaction between wastewater type, contact time, and adsorbent material, contact time, as shown in the interaction plot (Fig. 15). As the number of nonparallel lines increases, the interaction's potency increases (Mathialagan and Viraraghavan 2005). Based on this interaction effect, it was found that the level of each

parameter determined the relationship between parameters and phenol removal.

Interaction between adsorbent material and dose

Figure 15 shows that phenol removal efficiency varies significantly with adsorbent material and dose. *Phragmites australis* biochar (green dashed line) demonstrates a sharp increase in efficiency from 65% at 0.5 g/L to 80% at 6.5 g/L, attributed to a higher surface area (from 3.22 to 6.354 m²/g) and more adsorption sites, as confirmed by BET analysis. Activated carbon (blue solid line) also improves from 63 to 72% with increased dose, though it remains less effective than biochar due to comparatively limited pore size reduction and surface area increase. Li et al. (2020) support biochar's superior performance due to higher porosity.

Chitosan (red dashed line) shows a decline in efficiency from 66 to 62% as the dose increases due to particle aggregation reducing surface area and pore availability. SEM and BET analyses confirm that chitosan becomes less porous and smoother after adsorption. Su et al. (2024) and Zhang et al. (2023) similarly observed chitosan's lower efficiency, attributed to particle aggregation and blocked functional groups at higher doses, limiting adsorption in complex wastewater.

Interaction between wastewater type and contact time

As shown in Fig. 15, The interaction plot between Wastewater Type and Contact Time reveals that for WW Type 1 (likely oily wastewater), the phenol removal ratio remains relatively constant at around 63%, indicating that an increase in contact time from 20 to 90 min has minimal impact on removal efficiency. This minimal change can be explained by the high concentration of pollutants, including a COD of 1396.25 mg/L, BOD of 862.65 mg/L, and TDS

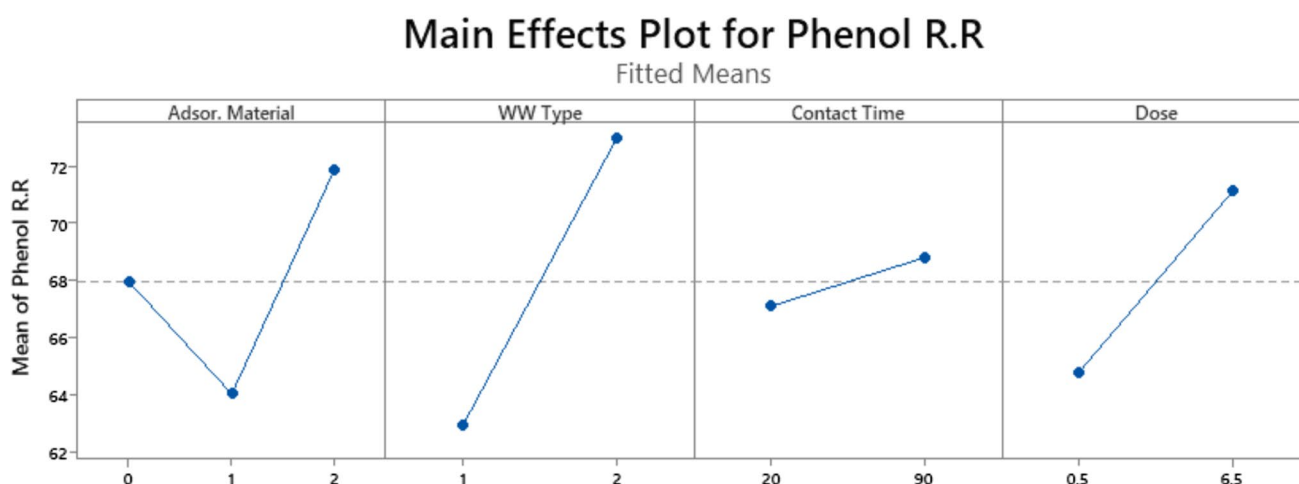


Fig. 14 The main effect plot of Phenol Removal

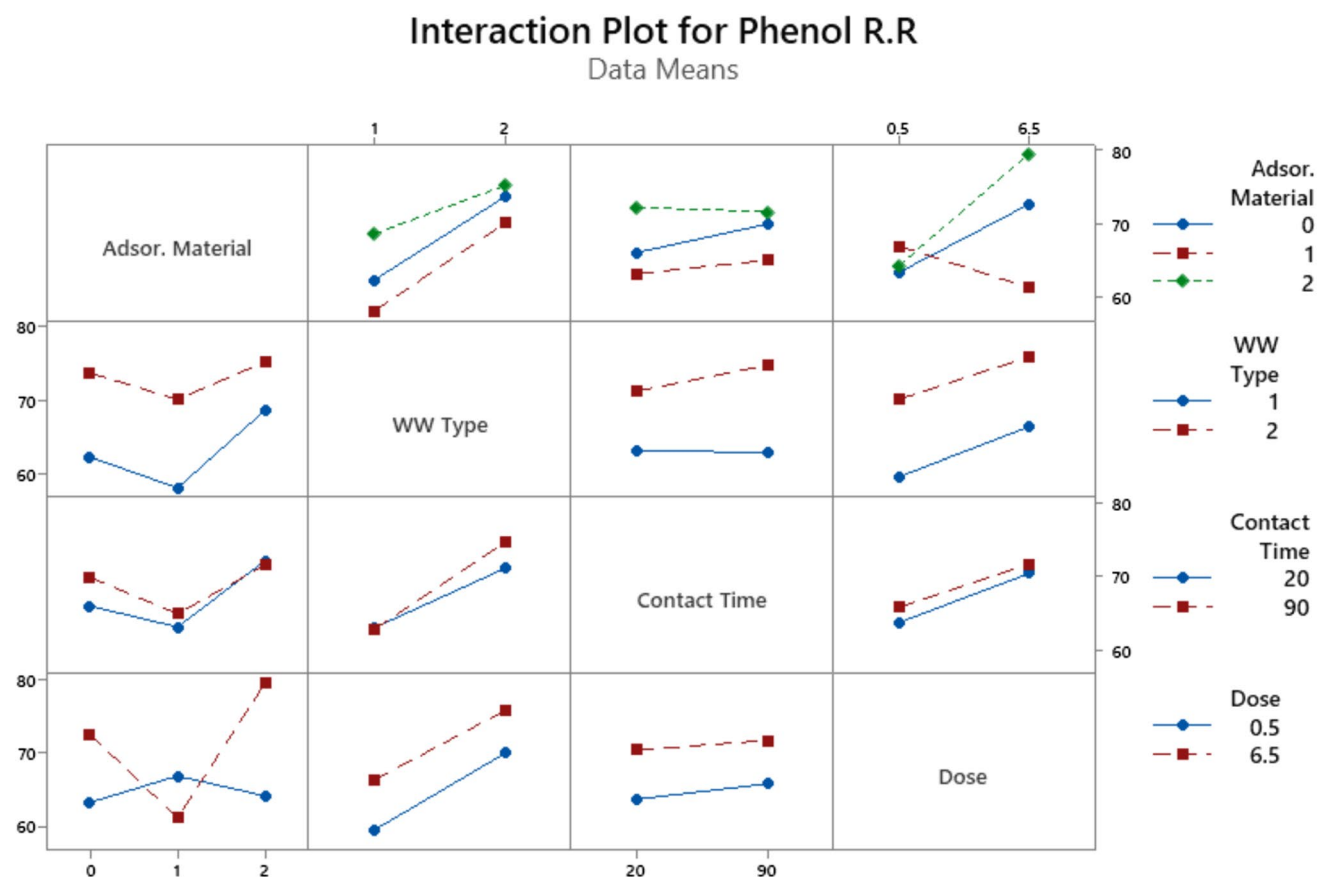


Fig. 15 Interaction plot for different parameters of Phenol Removal

of 1408 mg/L, combined with high turbidity (605.9 NTU). These characteristics of oily wastewater likely lead to the rapid saturation of the adsorbent's active sites, particularly due to the large organic molecules and oil present, which quickly block pores and hinder further phenol adsorption. Also, the viscosity of oily wastewater plays a critical role in limiting phenol removal efficiency over time. In contrast, for WW Type 2 (UASB effluent), the phenol removal ratio increases significantly from approximately 70–77% as contact time extends from 20 to 90 min. This can be attributed to the simpler composition of UASB effluent, which has lower pollutant levels, such as COD of 603 mg/L and BOD of 173.55 mg/L, and much lower turbidity (59.28 NTU). These characteristics allow for a more gradual saturation of the adsorbent, with phenol molecules continuing to adsorb over the extended contact time. The relatively low concentrations of organic matter and suspended solids in the UASB effluent provide better access to the adsorbent's surface, enabling continued phenol removal as contact time increases. Elbidi et al. (2021) similarly reported that biochar's porous structure allows for improved adsorption of phenol in oily wastewater, where other adsorbents struggle due to pore clogging by larger organic molecules. In contrast, (Kumar et al. 2020)

found that chitosan, while effective at lower phenol concentrations, exhibits reduced performance in oily wastewater due to its limited surface area and pore size, leading to faster saturation of adsorption sites. However, chitosan remains useful for phenol removal in less complex waste streams, such as UASB effluent, where competition for adsorption sites is lower.

Interaction between adsorbent material and wastewater type

Figure 15 reveals that phenol removal efficiency varies significantly with adsorbent material and wastewater type. In oily wastewater (WW Type 1), *Phragmites australis* biochar achieves the highest removal rate at 70%, followed by activated carbon at 63% and chitosan at 55%. For UASB effluent (WW Type 2), efficiency increases for all adsorbents: biochar reaches 79%, activated carbon 72%, and chitosan 70%.

Biochar performs better in UASB effluent due to its high surface area (6.354 m²/g) and strong functional group interactions (O–H, C=O), facilitating phenol adsorption. In oily wastewater, biochar's efficiency drops because larger organic molecules clog its pores, reducing access to adsorption sites.



Activated carbon and chitosan show lower efficiency due to weaker interactions with phenolic compounds and susceptibility to pore clogging. Zhang et al. (2023) confirmed biochar's superior performance in UASB effluent, achieving up to 80% removal efficiency, while (Li et al. 2020) noted that activated carbon's efficiency declines in complex wastewater (Khan et al. 2024). Further, it was observed that chitosan's weaker phenol interactions limit its effectiveness in oily wastewater compared to biochar and activated carbon.

Interaction between adsorbent material and contact time

Figure 15 illustrates how phenol removal efficiency varies with adsorbent material and contact time. *Phragmites australis* biochar maintains a high removal rate, starting at 73% at 20 min and slightly declining to 71% at 90 min, due to saturation of adsorption sites and pore blockage by larger organic molecules. EDX and BET analyses confirm this, showing reductions in pore volume (0.0377–0.0332 cc/g) and pore size (28.55–21.454 nm) over time. Activated carbon shows a positive trend, improving from 65% at 20 min to 70% at 90 min, suggesting enhanced adsorption with longer

contact. In contrast, chitosan has the lowest efficiency, marginally rising from 61 to 64%. Its smaller surface area (19.77 m²/g, decreasing to 17.002 m²/g) and reliance on hydrogen bonding via amine and hydroxyl groups limit its adsorption capability. Chen et al. (2020) confirmed biochar's superior performance, attributing it to higher surface area and functional groups (Li et al. 2020). We observed that activated carbon's efficiency improves with time, which is consistent with our findings (Khan et al. 2024). Noted chitosan's lower adsorption efficiency compared to biochar and activated carbon.

Numerical optimization

The desirability functions are shown in Fig. 16 represents the optimization process for maximizing COD and phenol removal under varying conditions of adsorbent material, wastewater type, contact time, and dose. The optimal conditions achieved a composite desirability of 0.9872, indicating a near-ideal balance for both responses. The maximum phenol removal (86.6766%) was attained with *Phragmites australis* biochar (Adsorbent Material 2), UASB effluent (WW

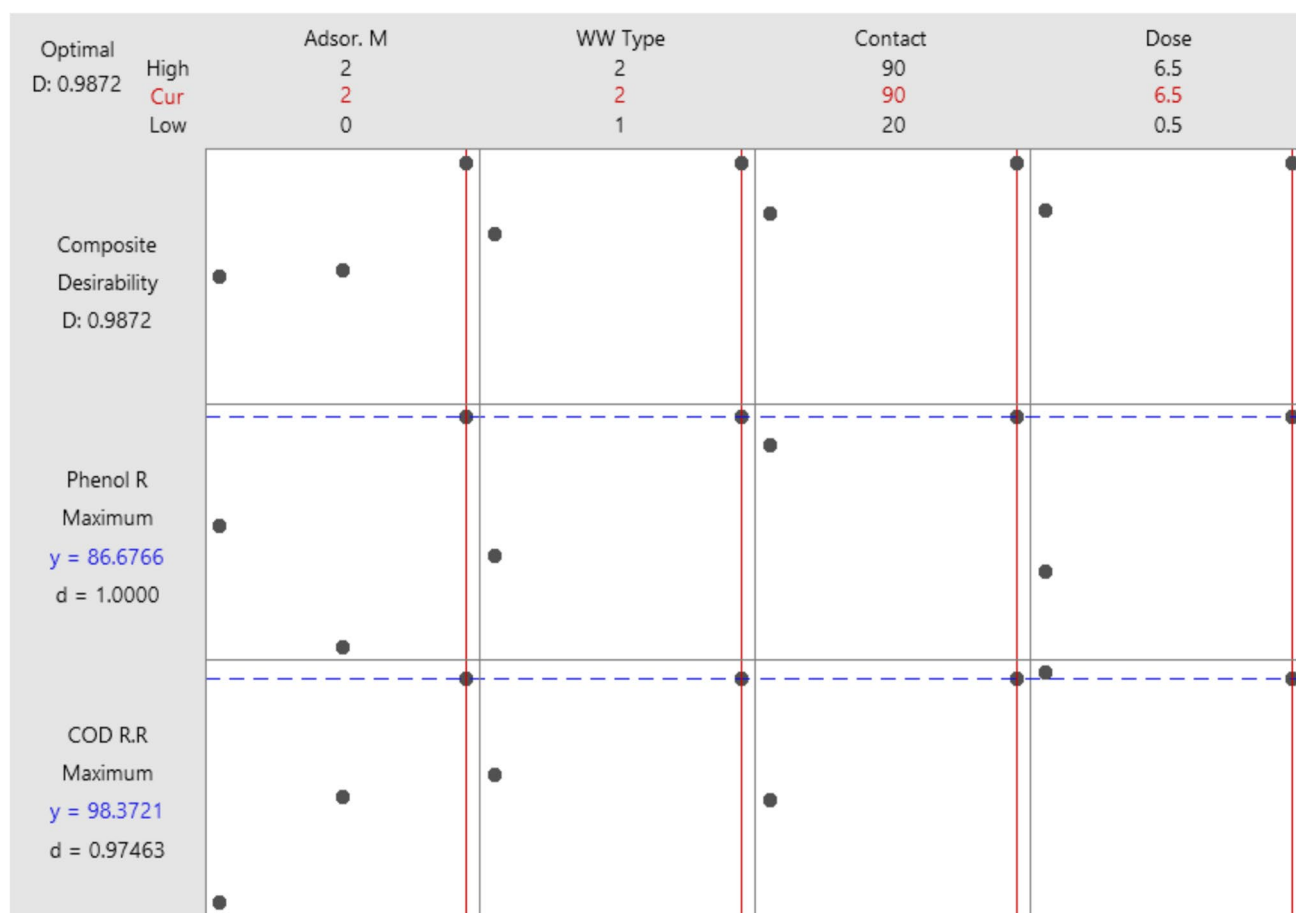


Fig. 16 Desirability functions for the optimization of COD and Phenol removal



Type 2), a contact time of 90 min, and a dose of 6.5 g/L, yielding a desirability value of 1.0000, which represents perfect optimization for phenol removal. For COD removal, the maximum rate of (98.3721%) was also achieved under the same optimal conditions, with a desirability value of 0.97463.

Performance comparison between industrial and domestic wastewater

This study primarily focused on UASB-treated agro-food industrial wastewater as a model system, employing *Phragmites australis* biochar and chitosan as sustainable, low-cost adsorbents due to their proven adsorption potential and environmental compatibility. While high removal efficiencies were achieved under these conditions, validating the performance of these materials across different wastewater matrices, such as domestic effluents, is critical to ensure broader applicability. Domestic wastewater often contains lower concentrations of organic pollutants but higher levels of biodegradable compounds, which may influence adsorption dynamics. To support this perspective, Table 9 provides a comparative overview of recent

studies conducted between 2019 and 2024 on adsorbent-based treatment of industrial and domestic wastewater, highlighting the diversity in adsorbent types, effluent characteristics, and removal efficiencies. This comparison underscores the need for extended evaluation of biochar and chitosan across varied treatment contexts.

Life cycle assessment

Goal and scope

The LCA aimed to compare and identify the most environmentally sustainable material for wastewater treatment. The functional unit was defined as the treatment of 1 m³ of wastewater. The system boundaries included producing adsorbent materials, their application in the wastewater treatment process, and the subsequent emissions, energy use, and resource consumption throughout the life cycle. End-of-life treatment of residuals was also considered. The best performance conditions for each adsorbent were selected based on COD removal efficiency.

Table 9 Recent studies on adsorbent-based treatment of industrial and domestic wastewater

No	Adsorbent material	Wastewater type	Target contaminants	Max removal (%)	Optimization/design approach	References
1	Coconut shell biochar	Distillery wastewater	COD, BOD	COD: 89%	RSM (Box-Behnken)	El-Mashad and Zhang (2019)
2	Activated carbon + TiO ₂	Petrochemical effluent	Phenol, COD	Phenol: 85%, COD: 78%	Taguchi Method	Rasheed et al. (2019)
3	Rice husk biochar	Food processing wastewater	COD, Phenol	COD: 92%, Phenol: 80%	Full Factorial Design	Huong et al. (2020)
4	Chitosan-modified bentonite	Dairy wastewater	COD, Turbidity	COD: 94%	Central Composite Design	Sharma et al. (2022)
5	Fe/Cu nanoparticles	Tannery wastewater	COD	COD: 93%	Multistage process: Fenton oxidation, coagulation, and nanotechnology	Naguib et al. (2024)
6	Biochar-based geopolymer nanocomposite	Domestic wastewater	COD, Phenol	COD: 92%, Phenol: 88%	Response Surface Methodology (RSM)	Jagaba et al. (2023)
7	Date palm fibres biochar (DPF600)	Synthetic domestic wastewater	Phenol	Up to 85%	Batch adsorption studies	Fseha et al. (2023)
8	Luffa cylindrical fibres (raw and NaOH-modified)	Synthetic phenolic wastewater	Phenol	Raw: 83.1%, Modified: 99.5%	Packed bed column experiments	Ogunniyi et al. (2024)
9	Biochar from various feedstocks	Anaerobically treated domestic wastewater	Micropollutants (including phenol)	Up to 100% for certain compounds	Adsorption studies	Hosney et al. (2025)
10	<i>Phragmites australis</i> biochar, chitosan, activated carbon	UASB-treated agro-food effluent	COD, Phenol	COD: 98.37%, Phenol: 86.68%	Full Factorial Design (Minitab 19)	Current Study 2024



Life Cycle Inventory (LCI)

The Life Cycle Inventory (LCI) phase involved quantifying all relevant material and energy inputs and emissions associated with the production and application of the three adsorbents. Activated carbon production requires significant energy and raw material inputs, primarily related to the high-temperature activation process. Chitosan production involves utilizing biowaste materials (shrimp shells) and substantial chemical and energy inputs during the deproteinization and deacetylation processes. *Phragmites australis* biochar was modeled as a low-input biomass-based material, requiring minimal energy and processing compared to the other adsorbents. Additionally, COD removal efficiencies achieved by each adsorbent were incorporated to normalize and adjust the environmental impacts associated with the treated effluent scenarios.

Life Cycle Impact Assessment (LCIA)

The Life Cycle Impact Assessment (LCIA) phase was carried out using the IMPACT 2002+ method. Key impact categories assessed included global warming potential, non-renewable energy consumption, human toxicity (carcinogens and non-carcinogens), respiratory effects, aquatic and terrestrial ecotoxicity, and land occupation. Figures 17 and 18 illustrate the environmental impact results and the process contribution analysis, respectively.

The results indicated that Activated Carbon consistently exhibited the highest environmental burdens, particularly in categories such as global warming potential, land occupation, and non-renewable energy use. Chitosan demonstrated moderate environmental impacts, with significant contributions arising from electricity consumption and thermal energy demand during its production and application. In contrast, *Phragmites australis* biochar consistently exhibited the lowest environmental impacts across all categories, attributed to its minimal processing requirements and the use of naturally available biomass.

It is important to note that Chitosan treatment of Arma wastewater resulted in higher environmental impacts compared to its use in treating UASB effluent, as shown in Fig. 17a, b. This difference is primarily due to the higher dosage required to achieve optimal COD removal in Arma wastewater (6.5 mg/L), compared to only 0.5 mg/L required for UASB effluent. The increased material and energy demand associated with the higher Chitosan substantially elevated the environmental impacts in the Arma treatment scenario.

Interpretation

The interpretation phase confirmed that *Phragmites australis* biochar offers the most environmentally sustainable option for wastewater treatment among the materials studied. The results show that using biochar significantly reduces greenhouse gas emissions, resource depletion, toxicity impacts, and energy use compared to Activated Carbon and Chitosan. While Chitosan is a biobased material that performs better than Activated Carbon, it still produces higher environmental impacts due to chemical usage and wastewater emissions during production. Therefore, the adoption of *Phragmites*-based biochar is recommended for sustainable wastewater treatment.

Conclusion

This research successfully demonstrates that *Phragmites australis* biochar serves as a high-performance, low-cost alternative to commercial activated carbon for the post-treatment of UASB effluent in agro-food industry wastewater. Using a multilevel factorial design, we systematically evaluated the influence of adsorbent type, dosage, contact time, and wastewater source on removing COD and phenol. The optimal conditions yielded removal efficiencies of 98.37% for COD and 86.68% for phenol, with *Phragmites australis* biochar outperforming both chitosan and activated carbon under these conditions. ANOVA results confirmed the statistical significance of adsorbent material, dosage, and wastewater type in determining treatment outcomes. By clearly identifying the most effective combination of sustainable adsorbents and operating parameters, this study fulfills its primary purpose of advancing environmentally friendly alternatives for industrial wastewater treatment. These findings support the integration of biochar-based media into scalable biofilter systems, reinforcing the broader goals of sustainable development, particularly SDG 6 (Clean Water and Sanitation) and SDG 12 (Responsible Consumption and Production). This study demonstrated that *Phragmites australis* biochar is a highly effective, low-cost alternative to commercial activated carbon for removing COD and phenol from wastewater. Using a factorial design, biochar achieved up to 98.37% COD and 86.68% phenol removal under optimal conditions. Key factors influencing removal efficiency were identified, with ANOVA highlighting the significance of wastewater type, adsorbent material, and dosage. The *Phragmites australis* biochar offers the most environmentally sustainable option for wastewater treatment. It significantly reduces greenhouse gas emissions, resource depletion, toxicity impacts, and energy use compared to Activated Carbon and Chitosan.



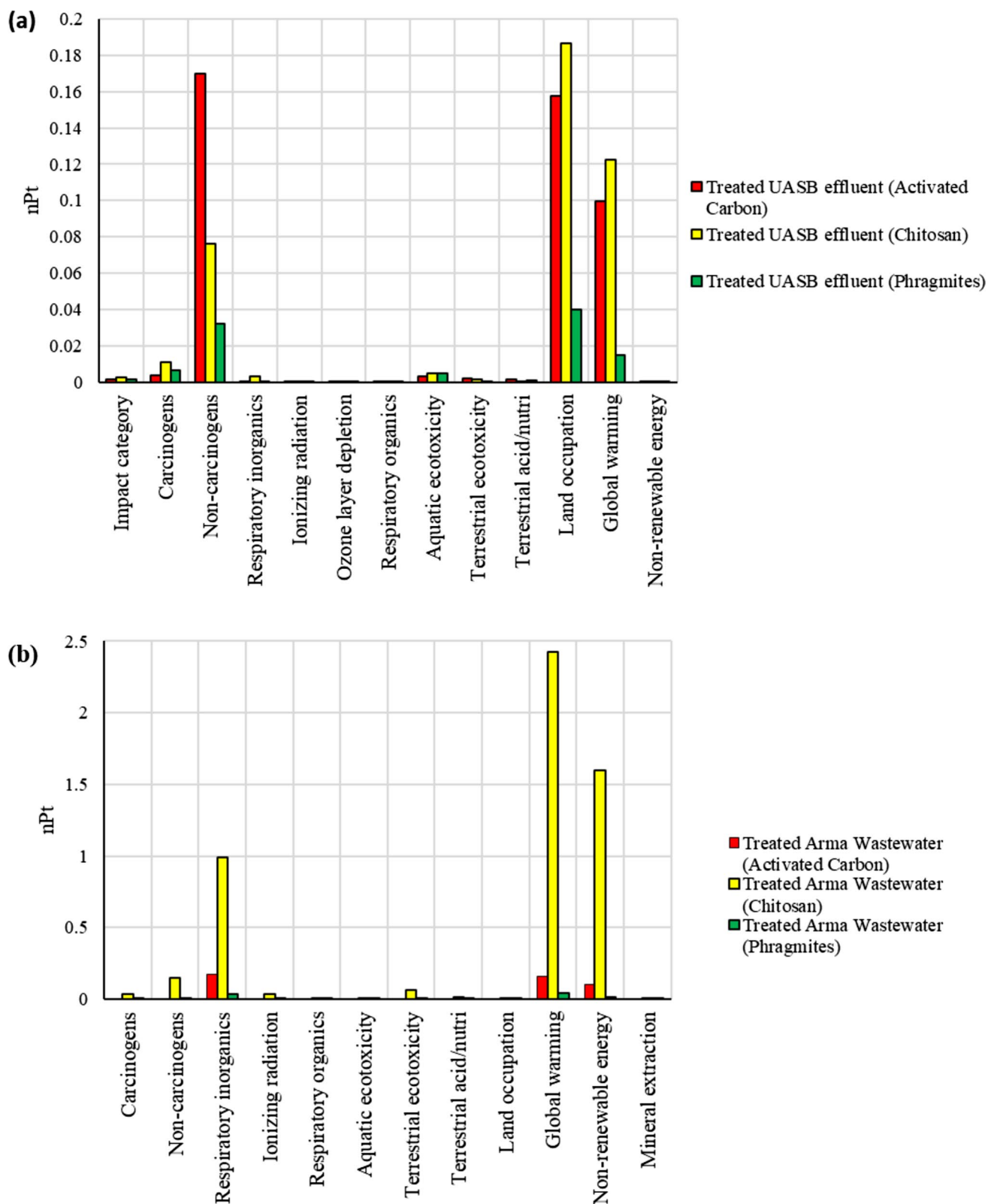


Fig. 17 Comparison impact assessment weighting of using activated carbon, chitosan, and *phragmites australis* biochar in treating **a** UASB effluent, and **b** Arma wastewaters using the IMPACT 2002+ Method

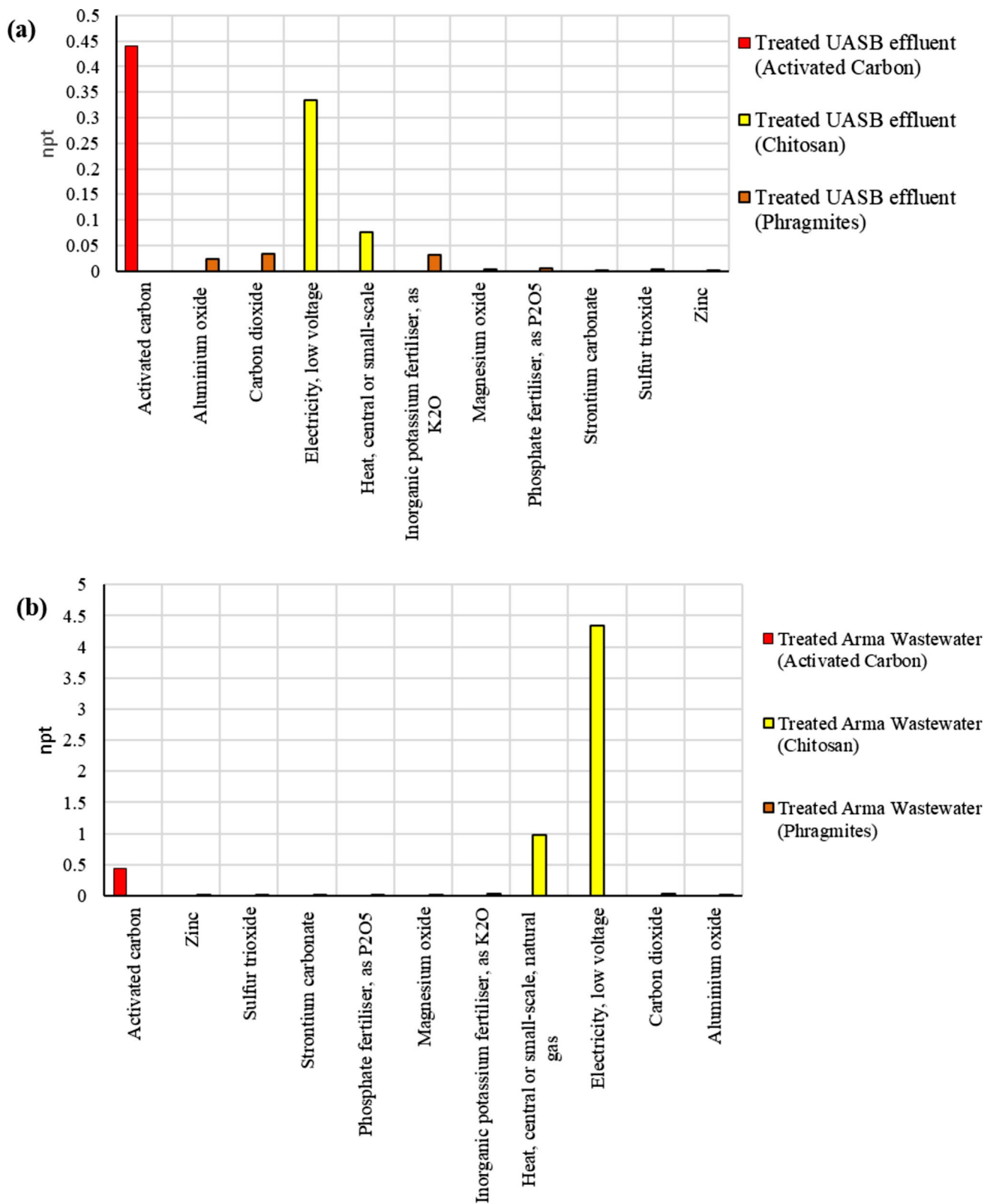


Fig. 18 Process contribution of using Activated Carbon, Chitosan, and *Phragmites australis* Biochar in Treating **a** UASB effluent and **b** Arma Wastewaters



Future work

Although this study establishes the effectiveness of *Phragmites australis* biochar as a sustainable and efficient adsorbent for the post-treatment of UASB effluent, several avenues remain for future research to enhance real-world applicability. First, pilot-scale studies are essential to validate laboratory findings under dynamic, real-world conditions. Such studies would help assess scalability, operational challenges, and cost-effectiveness in continuous treatment systems used in the agro-food industry. Second, long-term evaluations are necessary to examine the durability and reusability of biochar over multiple adsorption–desorption cycles. Investigating regeneration techniques (e.g., thermal or chemical methods) and assessing performance degradation over time will provide critical insights into biochar-based systems' economic and environmental sustainability. Third, future optimization efforts should consider advanced modeling techniques, such as response surface methodology (RSM), artificial neural networks (ANN), or genetic algorithms, to further refine process conditions and improve removal efficiency. Expanding the parameter set to include pH, temperature, flow dynamics, and competing pollutants would improve robustness and consistency across varying industrial scenarios.

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Author contributions AS, AM, MS, and SS initiated the study. AS, AM, MS, SS, KR, RW, and AS collected the materials and drafted the manuscript, which was critically commented on by AM, MS, SS, KR, RW, and AS and further thoroughly revised by AS. All the authors reviewed the manuscript.

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Declarations

Conflict of interest The authors have no competing interests to declare relevant to this article's content.

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References

- Abdel-Shafy HI, Mansour MS (2018) Solid waste issue: sources, composition, disposal, recycling, and valorization. Egypt J Pet 27(4):1275–1290. <https://doi.org/10.1016/j.ejpe.2018.07.003>
- Abedi T, Mojiri A (2019) Constructed wetland modified by biochar/zeolite addition for enhanced wastewater treatment. Environ Technol Innov 16:100–472. <https://doi.org/10.1016/j.eti.2019.100472>
- Abotaleb A, Saleh AM, Ali SE, Barakat NA, EL-Shatoury S, Shaltout A, El Shahawy A (2024) Boosting the performance of microbial fuel cells fed with partially treated buffalo milkmaid wastewater using modified CC/Co anodes: bacterial activity insights. Sustain Energ Fuels 8(17):3994–4005. <https://doi.org/10.1039/D4SE00792A>
- Apha (1985) Standard methods for the examination of water and wastewater: Apha
- Chaudhary N, Balomajumder C, Agrawal B, Jagati VS (2015) Removal of phenol using fly ash and impregnated fly ash: an approach to equilibrium, kinetic, and thermodynamic study. Sep Sci Technol 50(5):690–699. <https://doi.org/10.1080/01496395.2014.958170>
- Chen H, Zhou Y, Wang J, Lu J, Zhou Y (2020) Polydopamine-modified cyclodextrin polymer as efficient adsorbent for removing cationic dyes and Cu²⁺. J Hazard Mater 389:121897. <https://doi.org/10.1016/j.jhazmat.2019.121897>
- Chernicharo C, Van Lier J, Noyola A, Bressani RT (2015) Anaerobic sewage treatment: state of the art, constraints and challenges. Rev Environ Sci Biotechnol 14:649–679. <https://doi.org/10.1007/s1157-015-9377-3>
- Collivignarelli MC, Abba A, Caccamo FM, Calatroni S, Torretta V, Katsoyiannis IA, Rada EC (2021) Applications of up-flow anaerobic sludge blanket (UASB) and characteristics of its microbial community: a review of bibliometric trend and recent findings. Int J Environ Res Public Health 18(19):10326. <https://doi.org/10.3390/ijerph181910326>
- Dai X, Fang J, Li L, Dong Y, Zhang J (2019) Enhancement of COD removal from oilfield-produced wastewater by combination of advanced oxidation, adsorption and ultrafiltration. Int J Environ Res Public Health 16(17):3223. <https://doi.org/10.3390/ijerph16173223>
- Dos Santos PR, de Souza Leite L, Daniel LAJ (2022) Performance of biological activated carbon (BAC) filtration for the treatment of secondary effluent: a pilot-scale study. J Environ Manag 302:114026. <https://doi.org/10.1016/j.jenvman.2021.114026>
- El-Mashad HM, Zhang R (2019) Advances in plant-based waste-to-energy conversion technologies. Byprod Agric Fish Adding Value Food Feed Pharm Fuels. <https://doi.org/10.1002/9781119383956.ch16>
- El Shahawy A, Heikal G (2018a) Organic pollutants removal from oily wastewater using clean technology economically, friendly biosorbent (*Phragmites australis*). Ecol Eng 122:207–218. <https://doi.org/10.1016/j.ecoleng.2018.08.004>
- El Shahawy A, Heikal G (2018b) Regression, kinetics and isotherm models for biosorption of organic pollutants, suspended and dissolved solids by environmentally friendly and economical dried *Phragmites australis*. RSC Adv 8(71):40511–40528. <https://doi.org/10.1039/C8RA07221C>



- El Shahawy A, Mohamed A, Sahar E-S, Ahmed D, Aboulfotouh A, Dohdoh A, Gough HL (2024) Using *phragmites australis* biochar bio-augmented with *actinomyces* for enhancing UASB reactor performance: a field study. *J Water Process Eng* 68:106461. <https://doi.org/10.1016/j.jwpe.2024.106461>
- Elbidi M, Hewas A, Asar R, Mohd Salleh MSA (2021) Comparative study between activated carbon and biochar for phenol removal from aqueous solution. *BioResources*. <https://doi.org/10.15376/biores.16.4.6781-6790>
- Fisher TM, dos Santos AJ, Garcia-Segura SJ (2025) Recent advances and prospective challenges of iron metal-organic framework (MOF) catalysts in electrochemical fenton treatment technologies. *Curr Pollut Rep* 11(1):1–18. <https://doi.org/10.1007/s40726-024-00330-w>
- Fseha YH, Shaheen J, Sizzirici B (2023) Phenol contaminated municipal wastewater treatment using date palm frond biochar: optimization using response surface methodology. *Emerg Contam* 9(1):100202. <https://doi.org/10.1016/j.emcon.2022.100202>
- Gupta AK, Singh A, Saidulu D, Srivastava A, Rawat A (2024) Hybrid approaches for the mineralization of toxic chemicals. In: Dubey KK, Pant KK, Pandey A, Sanromán MÁ (eds) *Biodegradation of toxic and hazardous chemicals*. CRC Press, Boca Raton, pp 120–149. <https://doi.org/10.1201/9781003391494-7>
- Halalshah MM, Muhsen HH, Shatanawi KM, Field JA (2010) Improving solids retention in up-flow anaerobic sludge blanket reactors at low temperatures using lamella settlers. *J Environ Sci Health* 45(9):1054–1059. <https://doi.org/10.1080/10934529.2010.486329>
- Hameed BH (2009) Spent tea leaves: a new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions. *J Hazard Mater* 161(2–3):753–759. <https://doi.org/10.1016/j.jhazmat.2008.04.019>
- Han H, Rafiq MK, Zhou T, Xu R, Mašek O, Li XJ (2019) A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants. *J Hazard Mater* 369:780–796. <https://doi.org/10.1016/j.jhazmat.2019.02.003>
- Hazreen-Nita MK, Kari ZA, Mat K, Rusli ND, Sukri SAM, Harun HC, Nur-Nazifah M (2022) Olive oil byproducts in aquafeeds: opportunities and challenges. *Aquac Rep* 22:100–998. <https://doi.org/10.1016/j.aqrep.2021.100998>
- Heikal G, El Shahawy A (2019) Biosorption of phosphorus, total suspended and dissolved solids by dried *Phragmites australis*: isotherm, kinetic and interactive response surface methodology (IRSM) in oil and soap-derivatives industrial wastewater. *Desalination Water Treat* 137:243–259. <https://doi.org/10.5004/dwt.2019.23183>
- Hosney H, ElShourbagy M, Abdelrady A, Wagner T, Borén E, Ahmed M, Lens PN (2025) Micropollutant removal from domestic wastewater effluent by softwood-biochar and sludge-biochar for safe reuse applications. *Water Reuse*. <https://doi.org/10.2166/wrd.2025.095>
- Huong PT, Jitae K, Al Tahtamouni T, Tri NLM, Kim H-H, Cho KH, Lee C (2020) Novel activation of peroxydisulfate by biochar derived from rice husk toward oxidation of organic contaminants in wastewater. *J Water Process Eng* 33:101037. <https://doi.org/10.1016/j.jwpe.2019.101037>
- Jagaba AH, Lawal IM, Ghfar AA, Usman AK, Yaro NSA, Noor A, Birniwa AH (2023) Biochar-based geopolymer nanocomposite for COD and phenol removal from agro-industrial biorefinery wastewater: kinetic modeling, microbial community, and optimization by response surface methodology. *Chemosphere* 339:139620
- Jaiswal S, Kumar Gupta G, Panchal K, Mandeep, Shukla P (2021) Synthetic organic compounds from paper industry wastes: integrated biotechnological interventions. *Front Bioeng Biotechnol* 8:592939
- Khan R, Haram Z, Ahmad W, Sohni S, Xu J, Ilyas M (2024) Removal of hydrocarbon pollutants from refinery wastewater using N-hexadecyl chitosan as an efficient adsorptive platform. *Sci Rep* 14(1):17236
- Koyuncu H, Kul A, Akyavaşoğlu Ö (2025) Removal of heavy metals using lichen-derived activated carbons: adsorption studies, machine learning, and response surface methodology approaches. *Int J Environ Sci Technol* 22(7):5947–5968
- Kumar AKR, Saikia K, Neeraj G, Cabana H, Kumar VV (2020) Remediation of bio-refinery wastewater containing organic and inorganic toxic pollutants by adsorption onto chitosan-based magnetic nanosorbent. *Water Qual Res J* 55(1):36–51
- Li L, Kong Z, Xue Y, Wang T, Kato H, Li Y-Y (2020) A comparative long-term operation using up-flow anaerobic sludge blanket (UASB) and anaerobic membrane bioreactor (AnMBR) for the upgrading of anaerobic treatment of N, N-dimethylformamide-containing wastewater. *Sci Total Environ* 699:134370
- Loh ZZ, Zaidi NS, Syafiuddin A, Yong EL, Boopathy R, Hong Kueh AB, Prastyo DD (2021) Shifting from conventional to organic filter media in wastewater biofiltration treatment: a review. *Appl Sci* 11(18):8650
- Ma Y, Qian L, Huang H, Yang X (2006) Buildup of gold nanoparticle multilayer thin films based on the covalent-bonding interaction between boronic acids and polyols. *J Colloid Interface Sci* 295(2):583–588
- Mathialagan T, Viraraghavan TJ (2005) Biosorption of pentachlorophenol by fungal biomass from aqueous solutions: a factorial design analysis. *Environ Technol* 26(5):571–580
- Mishra SK, Chowdhury SD, Bhunia P, Sarkar AJ (2024) Clogging in subsurface flow constructed wetlands: mechanisms, influencing factors, measurements, modeling, and remediation. *Ecol Eng* 208:107–374
- Mohamed A, El-Shatoury S, Aboulfotouh A, El Shahawy A (2024a) Synergistic effects (adsorption and biodegradation) of *Streptomyces hydrogenans* immobilization on nano-reed biochar for further application in up-flow anaerobic sludge blanket. *RSC Adv* 14(32):22828–22846
- Naguib AM, Abdel-Gawad SA, Mahmoud AS (2024) Reduction of organic contaminants from industrial effluent using the advanced oxidation process, chemical coagulation, and green nanotechnology. *Sci Rep* 14(1):15221
- Ogunniyi S, Emenike EC, Iwuozor KO, Ighalo JO, Ezzat AO, Adewoye TL, Adeniyi AG (2024) Removal of phenol from wastewater using *Luffa cylindrica* fibers in a packed bed column: optimization, isotherm and kinetic studies. *Heliyon* 10(4):e26443. <https://doi.org/10.1016/j.heliyon.2024.e26443>
- Periyasamy APJS (2024) Recent advances in the remediation of textile-dye-containing wastewater: prioritizing human health and sustainable wastewater treatment. *Sustainability* 16(2):495
- Rasheed T, Adeel M, Nabeel F, Bilal M, Iqbal HM (2019) TiO₂/SiO₂ decorated carbon nanostructured materials as a multifunctional platform for emerging pollutants removal. *Sci Total Environ* 688:299–311
- Shaikh IN, Ahammed MMJWS (2022) Granular media filtration for on-site treatment of greywater: a review. *Water Sci Technol* 86(5):992–1016
- Sharma T, Xia C, Sharma A, Raizada P, Singh P, Sharma S, Nadda AK (2022) Mechano-chemical and biological energetics of immobilized enzymes onto functionalized polymers and their applications. *Bioengineered* 13(4):10518–10539
- Singh V, Singh J, Singh N, Verma MK, Praveena SM, Mishra V (2024) Sustainable removal of Pb(II) from aqueous medium by using chitosan functionalized *Citrus limetta* peels biomass. *Bioremediat J* 28(3):245–265
- Su X, Wang X, Ge Z, Bao Z, Lin L, Chen Y, Yang W (2024) KOH-activated biochar and chitosan composites for efficient adsorption of industrial dye pollutants. *Chem Eng J* 486:150387



- Tandukar M, Ohashi A, Harada H (2007) Performance comparison of a pilot-scale UASB and DHS system and activated sludge process for the treatment of municipal wastewater. *Water Res* 41(12):2697–2705
- Tao W, Duan W, Liu C, Zhu D, Si X, Zhu R, Pan B (2020) Formation of persistent free radicals in biochar derived from rice straw based on a detailed analysis of pyrolysis kinetics. *Sci Total Environ* 715:136–575
- Umar S, Elma M, Hidayat AS, Mahmud M, Rahma AJ (2025) Local and low-cost filter media of simple water filtration. *Water SA* 51(2):241–269
- Villegas LGC, Mashhadi N, Chen M, Mukherjee D, Taylor KE, Biswas N (2016) A short review of techniques for phenol removal from wastewater. *Curr Pollut Rep* 2:157–167
- Wald DM, Nelson KA, Gawel AM, Rogers HS (2019) The role of trust in public attitudes toward invasive species management on Guam: a case study. *J Environ Manag* 229:133–144
- Wang M, Bodirsky BL, Rijneveld R, Beier F, Bak MP, Batool M, Droppers B, Popp A, van Vliet MTH, Stokal M (2024) A triple increase in global river basins with water scarcity due to future pollution. *Nat Commun* 15(1):880
- Yadav A, Indurkar PD (2021) Gas sensor applications in water quality monitoring and maintenance. *Water Conserv Sci Eng* 6(3):175–190
- Zhang Y, Guo B, Dang H, Zhang L, Sun H, Yu N, Liu YJ (2022) Roles of granular activated carbon (GAC) and operational factors on active microbiome development in anaerobic reactors. *Bioresour Technol* 343:126104
- Zhang L, Chen Z, Zhu S, Li S, Wei C (2023) Effects of biochar on anaerobic treatment systems: some perspectives. *Bioresour Technol* 367:128226

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