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Influence of Thermal and Chemical Treatment on Biosorbent from Rice Husk and Its Application in Removal of Resorcinol from Industrial Wastewater

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Abstract: The removal of phenolic compounds is of great importance because of their toxic nature and potentially harmful effects on the environment and human health. This study examines the use of rice husk as a biosorbent for eliminating phenolic compounds, particularly resorcinol, from industrial wastewater. Three types of rice husk, namely raw rice husk (RRH), chemically treated rice husk (CTRH), and thermally treated rice husk (TTRH), are utilized after grinding and methanol treatment. Characterization techniques including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and optical microscopy are used to analyze the rice husk-based adsorbents. The microscopic analysis reveals the presence of nano-pores in TTRH and the existence of carbonyl and hydroxyl groups in all sorbent samples. XRD analysis confirms the presence of silica in biosorbents. This study also examines the influence of dosage and initial concentration on resorcinol sorption. Optimized dosages of 0.5 g (RRH), 0.5 g (CTRH), and 1.5 g (TTRH) result in sorption capacities of 14 mg/g (RRH), 11 mg/g (CTRH), and 5 mg/g (TTRH). Isotherm analysis indicates that the Langmuir isotherm best describes the sorption behavior of TTRH, while the Freundlich isotherm is observed for CTRH, and both RRH and CTRH follow the Temkin isotherm.

Keywords: rice husk; industrial wastewater; bio-adsorbent; phenolic compounds; optimal doses; environmental sustainability

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1. Introduction

Phenols are a class of chemical compounds consisting of an aromatic hydrocarbon group bounded by a hydroxyl group (-OH) directly. In organic chemistry, these compounds are also termed as phenolic. Phenol is the simplest compound of the class; it is sometimes called carbolic acid C_6H_5OH. Phenolic compounds are classified on the basis of the number of phenol units in the molecule, e.g., simple phenol, polyphenol, etc. These compounds are produced by plants and microorganisms with variations between species and are synthesized in industries [1–3]. Phenolic compounds possess a diverse range of physiological properties, including anti-allergenic, anti-atherogenic, anti-inflammatory, anti-microbial, antioxidant, anti-thrombotic, cardio-protective, and vasodilatory effects [1–3]. These compounds, found in fruits and vegetables, contribute to the antioxidant potential of foods and serve as natural sources of antioxidants [4]. They also play a significant role in the treatment and prevention of cancer, exerting chemo-preventive effects by influencing various cellular processes and signaling pathways [5,6].

Industrial development has allowed various chemicals to enter the natural environment and cause pollution. The presence of phenolic compounds in wastewater poses a threat to the environment, aquatic life, and human health and this issue must be catered to by applying an efficient treatment of wastewater [7–10]. Small quantities of chemicals, either naturally present in raw water or from industrial sources, or even produced during water treatment, can affect the organoleptic properties of drinking water [11]. These compounds are toxic even at very low concentrations, so it is recommended to decrease their concentration to a certain level before entering the wastewater stream. Some of the phenolic compounds were found to be remarkably harmful, such as resorcinol, etc. [12–14].

The anthropogenic sources of phenols are dyes, petrol, coal, chemical, fertilizer, and pharmaceutical industries [15]. It is necessary to eliminate these compounds from industrial effluents to prevent their hazardous effects and mitigate industrial wastewater pollution [8,10,16]. Resorcinol is classified as a hazardous substance and is highly combustible. Resorcinol serves as a versatile compound with various applications, including use as a coloring agent, antiseptic, disinfectant, and anti-itch agent [17,18]. Resorcinol is soluble in water, which poses a risk of it infiltrating waterways and harming aquatic life, making it an environmental hazard [19]. It is commonly found in the effluent waters of chemical, fertilizer, and dye industries, as well as coal conversion wastewater, contributing to water pollution [20]. It is characterized as a crystalline compound with a faint aromatic odor and a sweet taste [21]. Notably, resorcinol crystals exhibit triboluminescence, emitting light when subjected to mechanical stress [22,23]. Resorcinol, also known as 1,3-benzenediaol or 1,3-dihydroxybenzene, is a meta-isomer of benzene with the chemical formula $C_6H_4(OH)_2$. It has a relative molecular mass of 110.11 [21]. The chemical structure of it is shown in Figure 1. This structure represents the two hydroxyl (-OH) groups attached to the benzene ring at the meta positions (one and three positions).

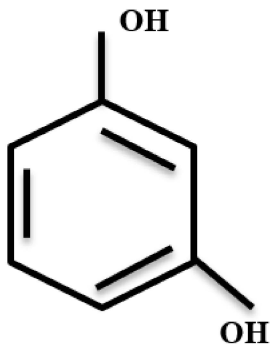


Figure 1. Chemical Structure of Resorcinol [22].

A number of techniques have been developed to remove the phenolic compounds from an aqueous solution including chlorination, solvent extraction, liquid membrane permeation, coagulation, chemical oxidation, and adsorption, etc. [24]. Among all these methods, adsorption is the most economical, effective, and simple method [16]. There are a number of techniques used for the removal of phenolic compounds from water. These techniques are divided into three main categories i.e., biological treatment, chemical treatment, and physical treatment [25].

Conventionally, biological treatment, activated carbon adsorption, and solvent extraction techniques are used. The physical adsorption technique is often thought to be the best, most viable, and frequently utilized strategy, which requires minimal effort, for the expulsion of phenolic compounds. Adsorption is a well-known separation process [26,27], which has a multitude of different applications, such as wastewater treatment, water desalination [28], pressure swing adsorption for the separation of gases [29,30], carbon capture and use [31], or production of cold in adsorption chillers [27,32], just to name a few. Adsorption has been found to be superior to other techniques for water reuse because of its low initial cost, flexibility and simplicity of design, ease of operation, and insensitivity to toxic pollutants [33].

The most popular and widely used adsorbent material for the treatment of wastewater is activated carbon [34,35]. Activated carbon present in powdered or granular form has a porous structure; these interconnected pores increase the surface area of carbon, thus making it the best adsorbent. But despite its great benefits, activated carbon is costly: the chemical and thermal regeneration of spent carbon is expensive, impractical on a large scale, produces additional effluent, and results in a considerable loss of the adsorbent [33]. So instead of this, there are many low-cost agricultural by-products that can be used as adsorbents for the treatment of wastewater. They include banana peel, orange peel, wheat straw, sawdust, powdered waste sludge, wheat shells, wheat bran, and hen feathers [9,33].

The purpose of our work is to investigate the efficiency of rice husk as an adsorbent for the removal of phenolic compounds from industrial wastewater. Rice husk is an abundant and low-cost agricultural waste residue and is easily available in large quantities. The effects of various operating parameters on adsorption such as sorbent dosage and contact time were monitored and optimal experimental conditions were determined [36,37]. Different adsorption isotherms (Langmuir and Freundlich isotherms) were used to find out the most suitable models describing our experimental findings. The nature of the substances and solution being studied is another factor to consider. Different adsorbates may have different chemical properties, such as polarity or molecular size, which can influence the adsorption process. Likewise, the characteristics of the solution, such as its pH or the presence of other ions, can also affect the adsorption behavior and the choice of the appropriate isotherm model [38,39].

2. Materials and Methods

2.1. Experimental Setup

For the experimentation, commercially available powdered rice husk was sieved using meshes ranging from 200 to 400 µm, and an average size was selected for the study. The sieved material was thoroughly washed with doubly deionized distilled water to remove fine particles and impurities. Three different methods were employed to treat the rice husk during the experimentation. Initially, the rice husk was washed and dried in an oven for 4 h to eliminate moisture. A portion of the dried rice husk was carefully stored in bottles to maintain its dry state and prevent moisture reabsorption [40,41].

During the experimentation, various equipment was utilized to facilitate the procedures and ensure accurate results. The weighing balance (Sartorius-TE214S, Cole Parmer, Goettingen, Germany) played a crucial role in precisely measuring the adsorbate and adsorbents. The jar test operator (Armfield WI-A, Cole Parmer) was employed for coagulation purposes, aiding in the treatment process. To analyze the phenolic compounds, a UV spectrophotometer (Shimadzu UV-1800, Cole Parmer) was utilized, enabling accurate and reliable measurements. Measuring cylinders were used for the preparation of samples, ensuring the appropriate volume for each experiment. Whatman Filter papers were employed for the filtration of samples, removing impurities, and facilitating the analysis. The sieve, categorized by the US standard mesh, enabled the sieve analysis of adsorbents, providing valuable information about their particle size distribution. The distiller (FAVORIT W4L, Cole Parmer) played a vital role in the distillation of water, ensuring its purity for the experiments. Additionally, a de-ionizer (Cole Parmer) was used to remove ions from the water, further enhancing its quality.

2.2. Experimental Methods

Adsorption isotherms are mathematical models used to describe the relationship between the concentration of adsorbate molecules in a solution and the amount of adsorbate adsorbed onto a solid adsorbent. Three commonly used types of adsorption isotherms are the Langmuir isotherm (Equation (1)), the Freundlich isotherm (Equation (4)), and the Temkin isotherm (Equation (7)) [42]. The Langmuir adsorption isotherm, developed by Langmuir, describes the adsorption of gases onto solid surfaces. It assumes a dynamic equilibrium between adsorbed and free gaseous molecules. Originally devised for gas–solid adsorption on activated carbon, it has been used to assess and compare various bio-sorbents. Langmuir's theory links the decline of intermolecular attractive forces to increasing distance [43].

$$q = \frac{q_m K_{ads} \times C}{1 + K_{ads} \times C} \tag{1}$$

where

q_e—sorbed concentration (adsorption density) (mg/g),
q_m—maximum capacity of adsorbent for adsorbate,
C—equilibrium concentration (mg/L),
K_{ads}—measure of affinity of adsorbate for adsorbent.
Linear form of Langmuir model [23] can be given by

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m \times K_{ads}} \tag{2}$$

$$\frac{C_e}{C_{ads}} = \frac{1}{Q_b} + \frac{C_e}{Q} \tag{3}$$

The Freundlich isotherm is an empirical equation describing the isothermal variation of gas adsorption per unit mass of solid adsorbent with pressure. It is the earliest relationship for non-ideal and reversible adsorption, applicable to both monolayer and multilayer adsorption. It accommodates the non-uniform distribution of adsorption heat and affinities on heterogeneous surfaces. This isotherm is widely used in heterogeneous systems, particularly for organic compounds or highly interactive species on activated carbon and molecular sieves [43]. Empirical equation is given by

$$q = K_f \times C^{\frac{1}{n}} \tag{4}$$

where

K_f—empirical Freundlich constant (L/g),
1/n—Freundlich exponent.
Linear form of Freundlich isotherm [23] is given by

$$log q_e = log K_f + \frac{1}{n} log\ Ce \tag{5}$$

or

$$log\ C_{ads} = log C_m + \frac{1}{n} log C_e \tag{6}$$

Temkin isotherm is the early model describing the adsorption of hydrogen onto platinum electrodes within the acidic solutions. The isotherm contains a factor that explicitly take into account the adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage [43,44]. Its empirical equation is given by

$$q_e = \frac{RT}{b} log(A * C_e) \tag{7}$$

Its linear form is

$$q_e = Blog(A) + Blog(C_e) \tag{8}$$

where

A = Temkin constant at equilibrium (L/g),

B = $\frac{RT}{b}$ = constant related to heat of sorption.

The selection of isotherms in adsorption studies depends on a range of factors. One important factor is the concentration of the adsorbate in the solution [40]. Different isotherm models may be more suitable for low or high concentration data ranges, and the choice of isotherm can affect the accuracy of the adsorption data.

In Figure 2, the methodology employed in this study, aimed at determining the optimum conditions for the adsorption process, is explained. Two key parameters, namely concentration and adsorbent dose, were investigated to identify the optimal values. The concentration of the phenolic compounds in the wastewater was varied to assess its impact on the adsorption efficiency. Different concentrations were evaluated to determine the optimum level that yielded the highest removal of phenolic compounds. Similarly, the adsorbent dose, representing the amount of rice husk used in the adsorption process, was studied to determine the ideal dosage for maximum adsorption efficiency. Various doses of the three types of rice husk (raw, chemically treated, and thermally treated) were evaluated to identify the optimal amount that resulted in the highest removal of phenolic compounds. The removal efficiency can be calculated using the following formulation:

$$Removal\ efficiency = \frac{(initial\ concentration\ -\ final\ concentration)}{initial\ concentration} \tag{9}$$

Furthermore, adsorption isotherms were employed to investigate the relationship between the adsorbate and adsorbent. The Langmuir isotherm, a monolayer adsorption model, has been utilized to determine the maximum adsorption capacity and the equilibrium constant for the adsorption process. The Freundlich isotherm, representing multilayer adsorption, has been used to understand the adsorption behavior in heterogeneous systems. Lastly, the Temkin isotherm, which considers the effects of heat and adsorbent-adsorbate interactions, has been applied to evaluate the energy changes during adsorption.

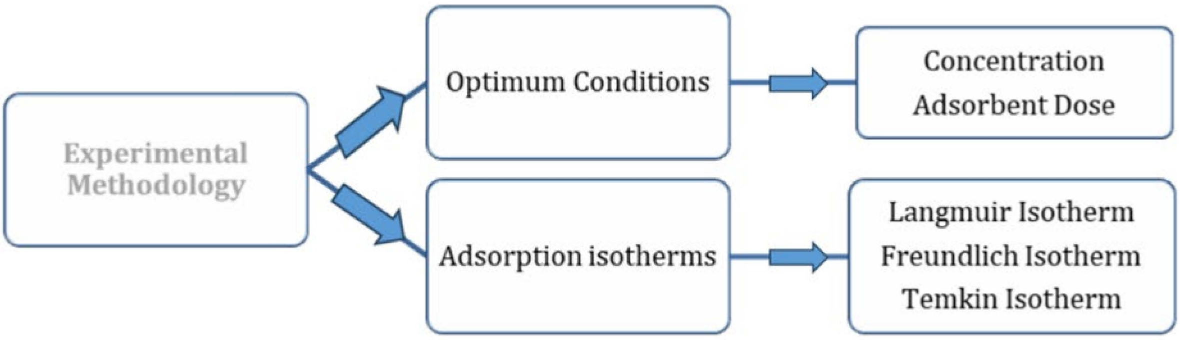


Figure 2. Experimental Methodology.

2.3. Preparation of Adsorbents and Adsorbate

Rice husks, the protective coatings of grains and seeds, consist of hard materials such as "opaline silica" and "lignin" that provide resilience during the growth period [23,41]. Due to its abundance and low cost, rice husk is currently being explored as a promising biomass. It contains cellulose, hemicellulose, and lignin as the main organic compounds [45]. This composition endows rice husk with excellent adsorbent properties, making it a promising candidate for pollutant removal applications [41,46].

In order to enhance the sorption properties of the rice husk, a series of treatment methods were applied. Initially, 200 g of dried rice husk underwent chemical treatment using 0.1 M nitric acid for 1 h, followed by a 4 h soak in methanol. This chemical treatment aimed to remove both organic and inorganic matter from the surface of the rice husk, thereby improving its sorption capabilities. Subsequently, 100 g of the chemically treated rice husk underwent thermal treatment. The husk was placed in a closed muffle furnace and exposed to a temperature of 400 °C for 1 h, resulting in a significant increase in its surface area. The resulting ash from the thermal treatment was utilized as the sorbent material in the study. These treatment methods yielded three distinct types of rice husk: raw or untreated rice husk, chemically treated rice husk, and thermally treated rice husk, each possessing unique properties for the subsequent sorption experiments.

Mainly, the current research study focused on the adsorption of phenolic compounds, specifically Resorcinol. Initially, a solution containing all phenolic compounds was prepared by thoroughly mixing them with 1000 mL of distilled deionized water. A flask was used to hold 0.1 g of the phenolic compounds, along with a portion of the water, which was then stirred using a magnetic stirrer. Gradually, the remaining water was added to the flask to create a 100 ppm solution. To enhance solubility, methanol and NaOH were introduced. From this stock solution, additional dilutions with desired concentrations (1, 3, 5, and 7 ppm) were prepared in 100 mL volumes. These dilutions were carefully selected to achieve the targeted concentrations for the experimental procedure.

2.4. Effect of Dose and Initial Concentration

To assess the impact of dosage on the removal efficiency of rice husk, the study employed four different doses of raw, chemically treated, and thermally treated rice husk. The sorbent doses, weighing 0.5 g, 1 g, 1.5 g, and 2 g, were accurately measured using a weighing balance. The prepared doses were placed in plastic bottles, each containing the same concentration. These bottles were then secured in a thermostatic shaker, set to operate at a speed of one hundred revolutions per minute (RPM), for a duration of 30 min. This process was repeated sequentially for raw rice husk, chemically treated rice husk, and, finally, thermally treated rice husk. Each type of rice husk dose was placed in separate bottles and subjected to the shaker treatment.

Subsequently, the samples were filtered using Whatman filter paper no. 40 to separate the solid sorbent from the liquid solution. The filtered samples were then injected back into the respective bottles. To create a stock solution with a concentration of 1 ppm, 1 mL of the solute was dissolved in 9 mL of solvent, and this solution was prepared in a separate bottle. The solutions, including the stock solution and the filtered samples, were analyzed using a UV spectrophotometer, utilizing a specific wavelength, to determine the removal efficiency of the rice husk sorbents. By following this experimental procedure, this study aimed to evaluate the influence of varying dosage on the effectiveness of raw, chemically treated, and thermally treated rice husk as sorbents.

This study involved the preparation of sorbent doses weighing 1 g each of raw, chemically treated, and thermally treated rice husk. Accurate measurements were taken using a weighing balance. These doses were then placed in plastic bottles containing adsorbate solutions of varying concentrations (1, 3, 5, and 7 ppm). To ensure consistent conditions, the bottles with the sorbent doses and adsorbate solutions were placed in a thermostatic shaker operating at 100 RPM for 30 min. This process was repeated for each type of rice husk sorbent, with the raw rice husk doses being used first, followed by the chemically treated and thermally treated rice husk doses. Subsequently, the samples were filtered using Whatman filter paper no. 40 to separate the solid sorbent from the liquid solution.

After filtration, the filtered samples were returned to their respective bottles for further analysis. Additionally, a stock solution of 1 ppm concentration was prepared by dissolving 1 mL of the solute in 9 mL of solvent, and this stock solution was also placed in a plastic bottle for analysis. All solutions, including the filtered samples and the stock solution, underwent analysis using a UV spectrophotometer at a specific wavelength [23].

2.5. Adsorption Isotherms

The adsorption isotherms provide valuable insights into the relationship between the concentration of the sorbate and its accumulation on the surface of the sorbent at a constant temperature [23]. To determine the maximum adsorption capacities of the adsorbents, experiments were conducted by varying the concentrations while keeping all other parameters constant. To study the isotherms, dilutions of 10, 20, and 30 ppm were prepared for raw rice husk, 10, 15, and 25 ppm for chemically treated rice husk, and 10, 15, 25, and 30 ppm for thermally treated rice husk. The optimum conditions determined for raw, chemically treated, and thermally treated rice husk were then applied in the experiments. In order to characterize the adsorbent materials, optical microscopy, Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) techniques were employed. These analyses provided valuable information on pore sizes, surface properties, and functional groups present in the rice husk, which play a crucial role in the adsorption process.

3. Results and Discussion

The main objective of this study was to determine the adsorption capacity of rice husks for the removal of phenolic compounds from solution. In order to investigate the sorption capabilities of rice husk, a series of experiments were conducted to optimize various parameters, including the sorbent dose and the initial concentration of the phenolic compound. By performing these experiments and analyzing the resulting isotherms, valuable insights into the adsorption behavior of rice husk and its effectiveness as an adsorbent were obtained. The adsorption kinetics were also investigated.

3.1. Characterization of Rice Husk Samples

Optical microscopy analysis was employed to gain valuable insights into the sizes of micro- or nanopores in the rice husk samples. The characterization of rice husk involved the use of three different techniques, and the results obtained are presented below in Figure 3a. In the case of both raw rice husk and chemically treated rice husk, a magnification of 5× was found to be more suitable (Figure 3a,b). For the analysis of thermally treated rice husk, an optimal magnification of 10× was determined in Figure 3c. Microscopic images show that the structure has been altered as a result of thermal treatment. On the other hand, the morphology of the chemically treated sample was similar to the raw sample, indicating that chemical treatment mostly influenced the surfaces from the perspective of functional groups (Figure 3d).

FTIR analysis identifies the chemical compounds present in consumer products, polymers, and in pharmaceutical products. It offers the quantitative and qualitative analysis of organic compounds. The FTIR analysis shown in the Figure 3d allowed the clear identification of OH, C=O, and C-OH functional groups. The OH group is typical for many different types of biomass, as it is relatively abundant in cellulose and hemicellulose [47].

The C=O group at 1725 cm^{-1} was also found by Wawrzkiewicz and Podkościelna [48] during studies on the sorption of auramine O basic dye using ethylene glycol dimethylacrylate-based microspheres. Electrostatic interaction between the dye molecule and the C=O functional group present at the surface of the microspheres has been proposed by Wawrzkiewicz and Podkościelna [48] as a part of the mechanism of interactions between the sorbent and the dye.

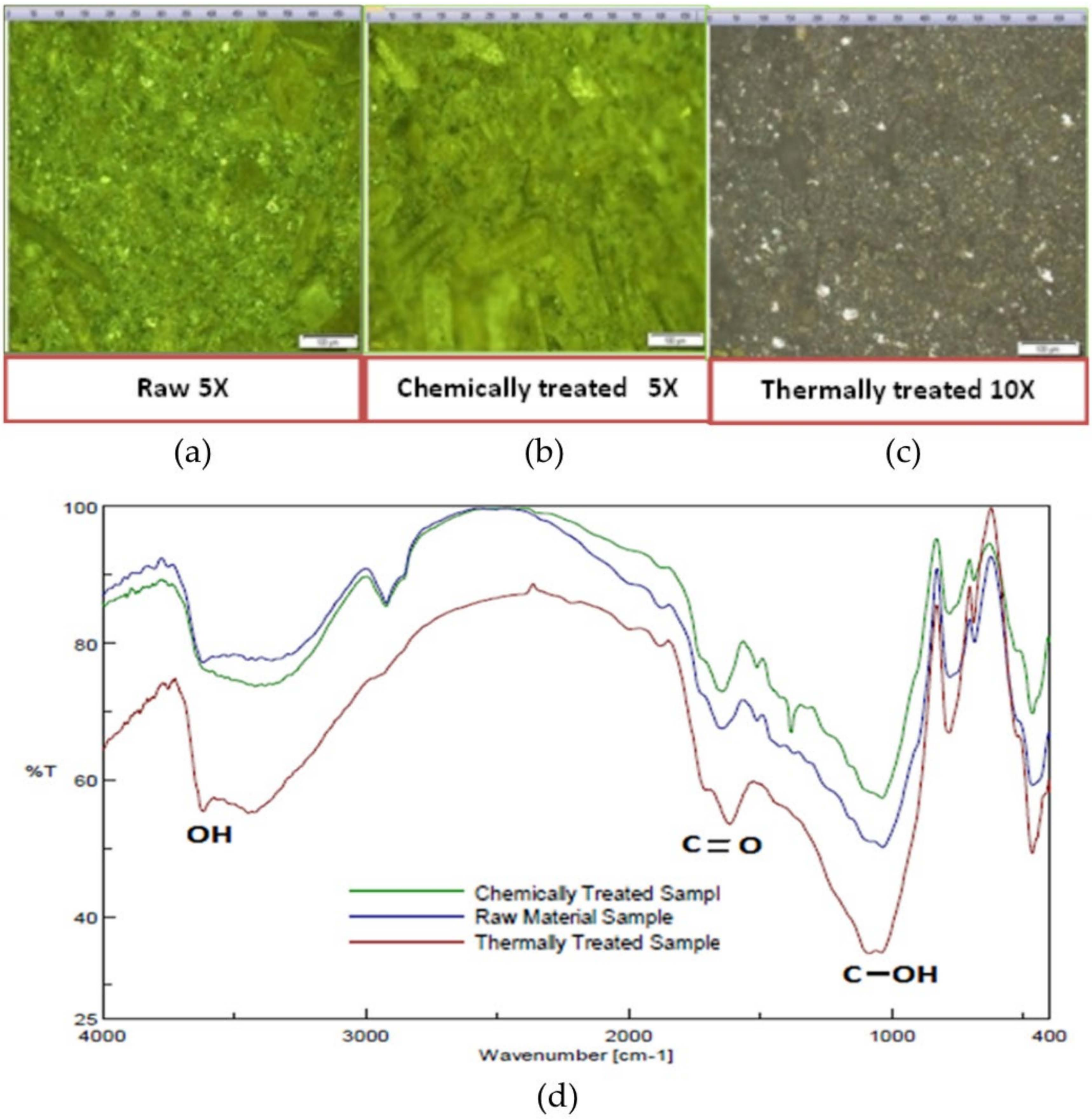


Figure 3. Chemically treated, raw materials and thermally treated samples using Optical Microscopy, results at (**a**) 5×, (**b**) 5×, (**c**) 10×, (**d**) FTIR Results.

XRD is a unique method used in determining the crystalline property of a compound. It is used for the characterization of various materials. XRD analysis shows that SiO_2 and Fe_3O_4 are major constituents that will monitor the adsorption phenomenon. The XRD analysis of raw, chemically treated, and thermally treated rice husk in Figure 4a–c revealed important structural changes induced by the treatment processes. The XRD patterns confirmed the presence of major constituents, SiO_2 (silicon dioxide) and Fe_3O_4 (iron (II, III) oxide), which are crucial for monitoring the adsorption phenomenon. Chemical treatment led to the degradation or removal of cellulose, hemicellulose, and lignin, resulting in changes in the XRD pattern and the formation of new phases. Thermal treatment further modified the XRD pattern, with significant degradation of the aforementioned components and the emergence of new peaks. These structural modifications, along with the presence of SiO_2 and Fe_3O_4, highlight the potential influence of the treatments on the adsorption capabilities of rice husk, emphasizing the need for further investigation into their role in phenolic compound removal.

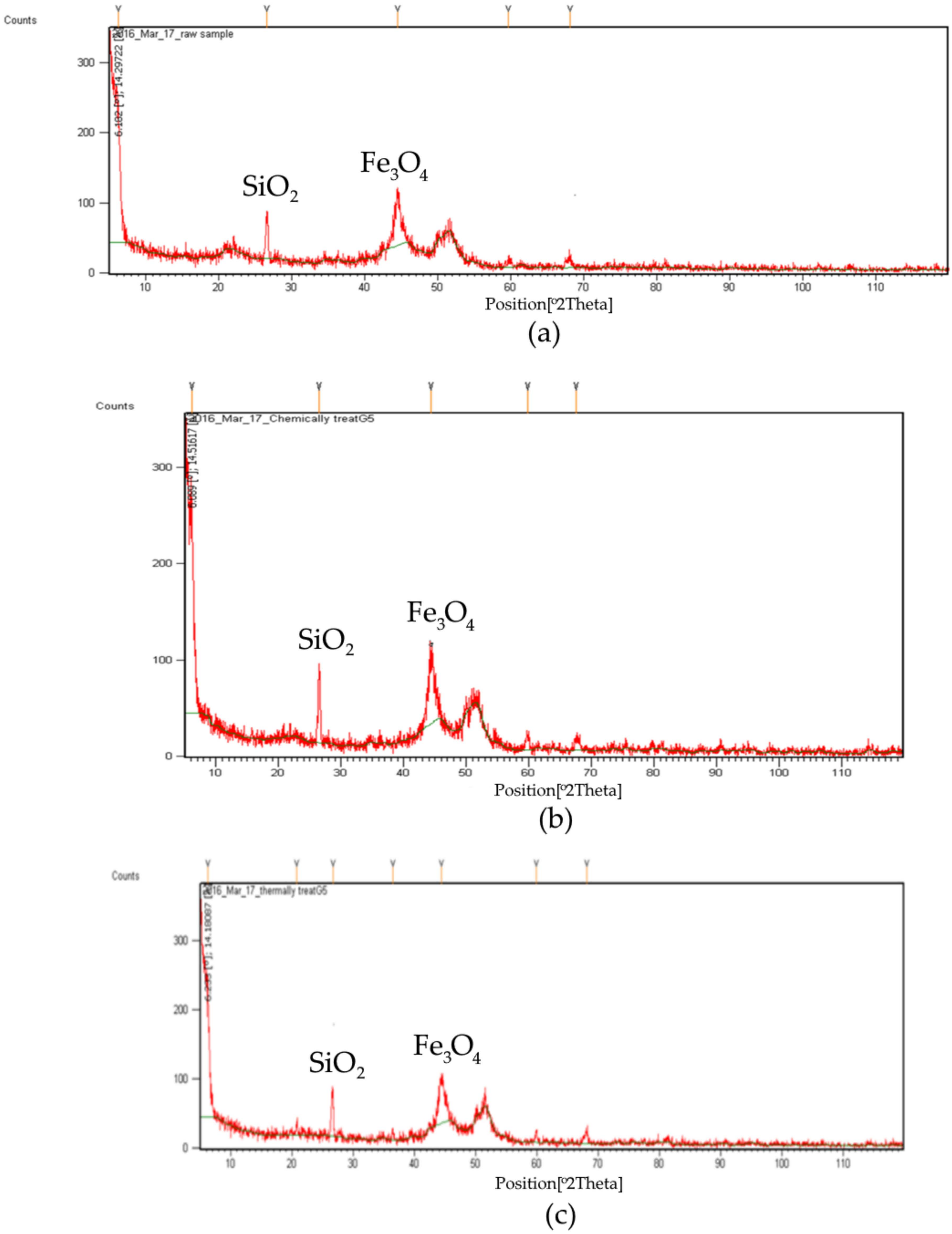


Figure 4. The XRD results for RRH (**a**), for CTRH (**b**), for TTRH (**c**).

Based on the experimental data, descriptive statistics and correlation analysis were conducted to explore the relationships and characteristics of the variables. Descriptive statistics provided insights into the central tendency and variability of the data, including mean, standard deviation, minimum, maximum, and quartiles for each variable within each group (Raw Rice Husk, Chemically Treated Rice Husk, Thermally Treated Rice Husk). The correlation analysis calculated correlation coefficients between the variables (m, q_e, $1/q_e$, C_e/q_e, $1/C_e$, $\log(q_e)$, $\ln(C_e)$) within each group, helping to identify relationships or dependencies between the variables. The correlation coefficients ranged from −1 to 1, where values close to −1 indicated a strong negative correlation, values close to 1 indicated a strong positive correlation, and values close to 0 indicated a weak or no correlation.

Table A1 presented the correlation analysis results as a heatmap, revealing the relationships between variables within each group. The Raw Rice Husk group showed several strong positive correlations, indicating positive linear relationships between variables such as m and q_e, $1/q_e$ and C_e/q_e, and $1/C_e$ and $\log(q_e)$. Conversely, strong negative correlations were observed between variables such as m and $1/C_e$, $1/q_e$ and $\log(q_e)$, and $1/C_e$ and $\ln(C_e)$, suggesting negative linear relationships. The variable q_e demonstrated high positive correlations with most other variables in this group.

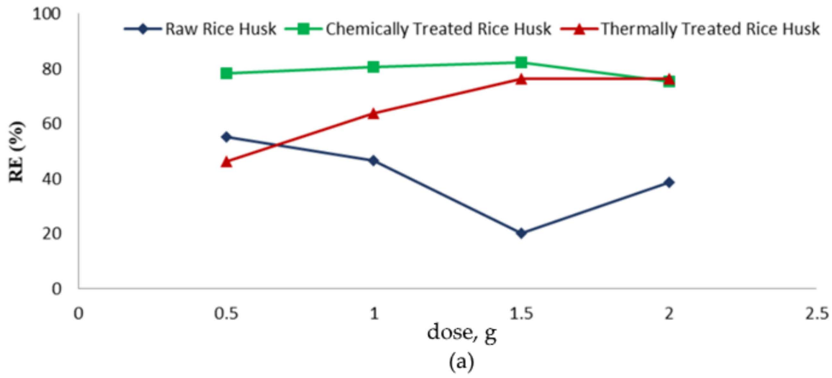
Similar patterns were observed in the Chemically Treated Rice Husk group, with strong positive correlations between m and q_e, $1/q_e$ and C_e/q_e, and $1/C_e$ and $\log(q_e)$, as well as strong negative correlations between m and $1/C_e$, $1/q_e$ and $\log(q_e)$, and $1/C_e$ and $\ln(C_e)$. The variable q_e also exhibited high positive correlations with the other variables in this group. In the Thermally Treated Rice Husk group, correlation patterns resembled those of the other groups. Strong positive correlations were observed between m and q_e, $1/q_e$ and C_e/q_e, and $1/C_e$ and $\log(q_e)$, along with strong negative correlations between m and $1/C_e$, $1/q_e$ and $\log(q_e)$, and $1/C_e$ and $\ln(C_e)$. The variable q_e displayed high positive correlations with the remaining variables in this group.

The regression analyses on the provided experimental data (Table A2) examined the relationships between independent variables and the dependent variable ($\ln(C_e)$) within three groups: Raw Rice Husk, Chemically Treated Rice Husk, and Thermally Treated Rice Husk. In the Raw Rice Husk group, m had a positive effect on $\ln(C_e)$ (estimate = 0.22909, p = 0.021), while q_e had a negative effect (estimate = −0.05373, p = 0.033). However, the variables $1/q_e$, C_e/q_e, $1/\mathrm{C_e}$, and $\log(q_e)$ did not significantly impact $\ln(C_e)$ ($p > 0.05$). Similarly, in the Chemically Treated Rice Husk group, "m" positively affected $\ln\mathrm{C_e}$ (estimate = 0.19237, p = 0.047), and q_e negatively affected $\ln(C_e)$ (estimate = −0.06816, p = 0.041). The other variables had no statistically significant impact ($p > 0.05$). In the Thermally Treated Rice Husk group, m showed a non-significant positive effect on $\ln(C_e)$ (estimate = 0.13906, p = 0.211), while q_e had a significant negative effect (estimate = −0.1607, p = 0.012). The remaining variables showed no statistically significant impact ($p > 0.05$).

The regression analyses revealed that m and q_e had significant effects on $\ln(C_e)$ in different groups. However, the variables $1/q_e$, C_e/q_e, $1/C_e$, and $\log(q_e)$ did not significantly predict $\ln(C_e)$ in any group. These findings provide valuable insights for optimizing adsorption conditions and dosage.

3.2. Optimum Conditions

Experiments and statistical analysis were performed to find the optimum conditions for the adsorption of phenolic compounds onto the rice husk. Optimum conditions included concentrations of adsorbate. The optimum dose of adsorbent for the adsorption of phenolic compound was found by experiments and confidante by co-relation and mul-polynomial regression. The experiments were performed by varying the dose of rice husk (raw, thermally treated, and chemically treated) from 0.5 g to 2.0 g while keeping all other parameters constant. Figure 5a represents the graph showing the removal efficiency of resorcinol at different doses of rice husk.



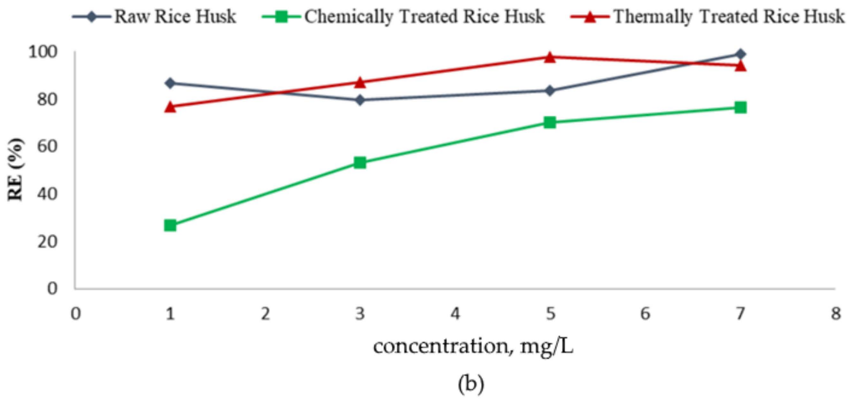


Figure 5. (**a**) Effect of dose on removal efficiency using RRH, CTRH, and TTRH (Concentration 15 ppm), (**b**) Effect of concentration on removal efficiency using RRH, CTRH, and TTRH (Dose −1 Gram).

The removal efficiency in the case of raw rice husk was higher at lower doses; when the dose was further increased a slight decrease in removal efficiency was observed. In the case of the chemically treated rice husk, no significant increase was observed in the removal efficiency when the dose was increased. On the other hand, in the case of the thermally treated rice husk, the removal efficiency increased significantly when the dose was increased. Overall, the maximum removal efficiency was observed at a dose of 1.5 g.

The removal rate was high when the dose was increased initially because the surface area provided by the adsorbent is high and a large number of sorption sites are present [49]. When the dose was increased further, no significant increase in removal efficiency was observed because the value of q_e decreased with an increase in adsorbent dosage, where q_e is the amount of resorcinol adsorbed on per unit weight of rice husk [50]. It can be explained by this that adsorption sites remain saturated during the adsorption process while the number of sites for adsorption increases by increasing the dosage. It has been observed that the adsorption of phenolic compounds is also influenced by the initial concentration of the adsorbate. The effect of initial concentration plays a crucial role in the removal or adsorption process. Figure 5b presented below illustrates the removal efficiency of the phenolic compound at different concentrations using three types of rice husk (raw, chemically treated, and thermally treated).

Several experiments were conducted while varying the initial concentration within the range of 1–7 mg/L, while keeping all other parameters constant, to determine the optimum concentration. The results obtained from the graphs indicate that as the concentration of the adsorbate increases, the removal efficiency also increases. Particularly for the chemically treated rice husk, a significant enhancement in removal efficiency is observed when the initial concentration varies from 1 to 7 mg/L. The highest removal efficiency is observed for the raw rice husk at 7 mg/L, while for the thermally treated rice husk, the highest removal efficiency is observed at 5 mg/L. These findings highlight the dependency of the adsorption process on the initial concentration of the phenolic compound. The results suggest that the adsorption capacity of the rice husk sorbents is influenced by the concentration of the adsorbate, with variations observed among the diverse types of rice husk treatments. This information aids in determining the optimal conditions for phenolic compound removal using rice husk-based sorbents.

This study examined the optimal conditions shown in the Table 1 for the effect of dose and initial concentration on the removal of resorcinol using different rice husk sorbents. For raw rice husk, the optimal dose was determined to be 0.5 g, and the optimum concentration was found to be 7 mg/L. Under these optimum conditions, the experimental results demonstrated a removal efficiency of 50% for resorcinol at the optimum dose and 90% at the optimum concentration. Similarly, for chemically treated rice husk, the optimal dose was identified as 0.5 g, and the optimum concentration was determined to be 7 mg/L. Experimental observations revealed a resorcinol removal efficiency of 70% under these optimal conditions. For thermally treated rice husk, the optimum dose was found to be 1.5 g, and the optimum concentration was determined to be 5 mg/L. The experimental results indicated that 80% of the resorcinol was removed from the solution under these optimal conditions. These findings highlight the importance of dose and initial concentration in the efficiency of resorcinol removal using different rice husk sorbents.

Table 1. Optimum conditions for the removal of resorcinol using RRH, CTRH, and TTRH.

Optimum Conditions	Raw Rice Husk	Chemically Treated	Thermally Treated
Dose (grams)	0.5	0.5	1.5
Concentration (mg/L)	7	7	5

3.3. Adsorption Isotherms

Adsorption isotherms graphically illustrate the adsorption behavior of adsorbate on specific adsorbents, showing the relationship between adsorbate amounts (x) and pressure at a constant temperature. Three isotherm models (Langmuir, Freundlich, Temkin) were used to describe the adsorption process mathematically. By varying adsorbate concentrations, experiments determined the maximum adsorption capacity of the adsorbents. Sorption isotherms relate resorcinol uptake per unit weight of rice husk (q_e) to the equilibrium adsorbate concentration in the liquid phase (C_e).

Figure 6a shows the Langmuir isotherm of resorcinol onto the rice husk. The Langmuir model was developed to represent the monolayer mechanism on a set of delocalized sorption sites. It gives the uniform energies of monolayer sorption onto the adsorbent surface [23]. The values of q_m and k_{ads} are evaluated from the slope and intercept of the plot between $1/q_e$ and $1/C_e$ as shown in Figure 6 [51]. The values of the Langmuir isotherm constants are given in Table 2. The value of R^2, which is called the coefficient of determination, is greater for thermally treated rice husk (close to 1) for the Langmuir isotherm. The value of k_{ads} is less in the case of raw rice husk; it means that the affinity of adsorbate is less for raw rice husk. The affinity of resorcinol is greater for chemically treated rice husks. The value of q_m, which indicates the capacity of adsorbent [52] for specific adsorbate, is greater for thermally treated rice husk. The raw rice husk has less capacity for adsorbate. If the thermally treated rice husk has a greater value of R^2, it means that the Langmuir isotherm is best followed by this type of rice husk.

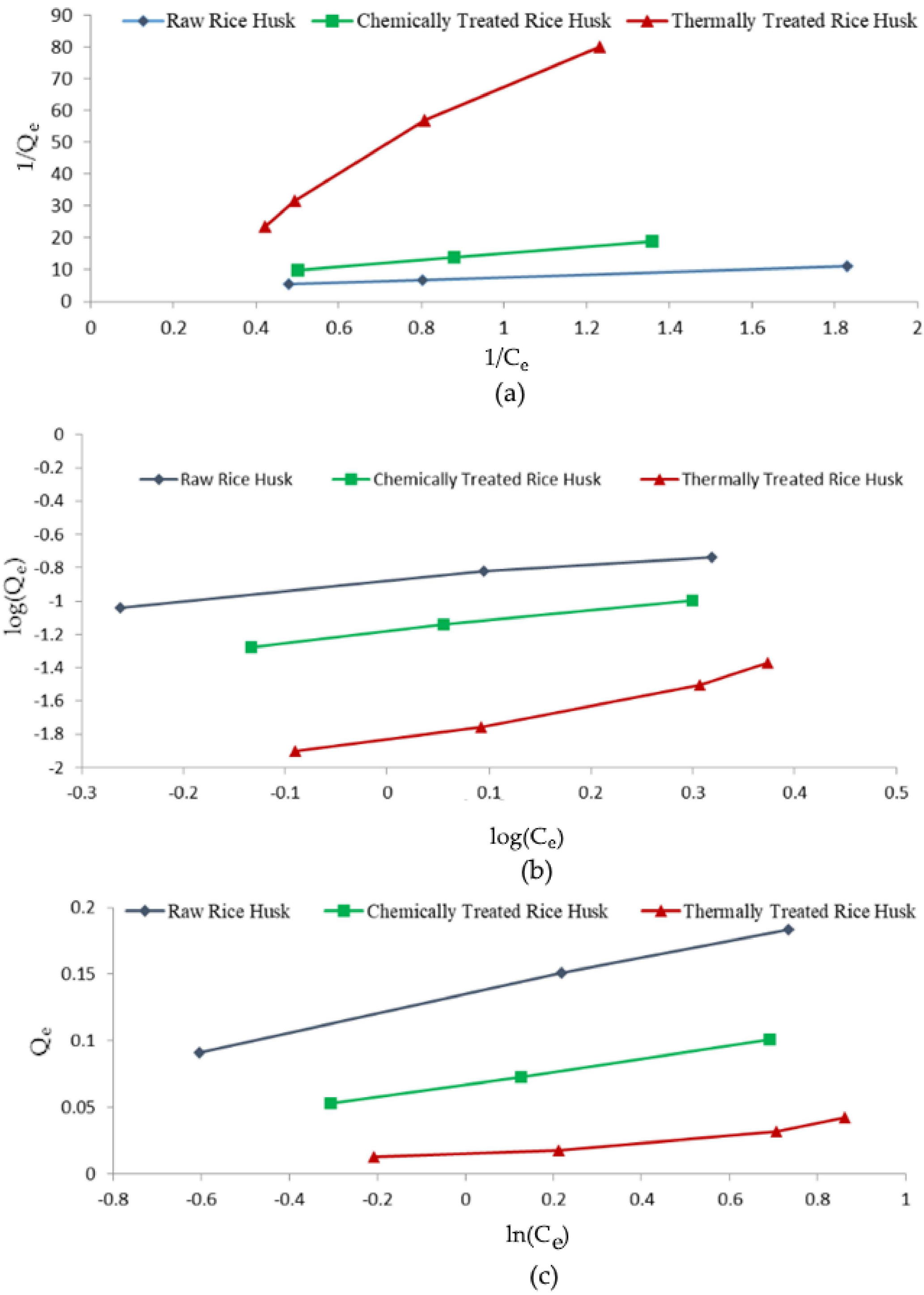


Figure 6. Different isotherm using RH, CRH, and TRH (**a**) Langmuir isotherm, (**b**) Freundlich isotherm, (**c**) Temkin isotherm.

Table 2. Parameter values for isotherms.

Constants	Langmuir Isotherm		
	Raw Rice Husk	**Chemically Treated**	**Thermally Treated**
R^2	0.986	0.995	0.999
K_{ads}	−23.99	2.30	1.24
Q_m	0.01	0.09	0.24
	Freundlich isotherm		
R^2	0.984	0.995	0.982
K_f	0.13	0.07	0.01
N	1.87	1.55	0.89
	Temkin isotherm		
R^2	0.998	0.9995	0.924
A	6.83	4.03	1.79
B	0.07	0.05	0.03

The Freundlich isotherm is the most widely used isotherm model or empirical expression that describes the surface heterogeneity and exponential distribution of active sites of adsorbent and their energies towards adsorbate. It follows the multilayer sorption mechanism [23]. The values of the constants of the Freundlich isotherm are given in Table 2. These constants are evaluated from the intercept and slope of the plot between log(Q_e) and log(C_e) in Figure 6b. The value of R^2 is greater for chemically treated rice husks. It shows that the Freundlich isotherm is best followed by the chemically treated rice husk. The value of K_f, which is the empirical Freundlich constant (capacity factor, L/g), is greater for raw rice husk and lowest for thermally treated rice husk. The value of n, which is the measure of affinity for the adsorbate, is greater for raw rice husk and the least for thermally treated rice husk. The Freundlich isotherm is best followed by chemically treated rice husk.

The graph of the Temkin isotherm model is shown in Figure 6c. The values of constants A and B were found by the slope and intercept of the plot between Q_e and $\ln C_e$ given in Table 2. The value of R^2 is greater for both raw and chemically treated rice husk. The value of A, which is the capacity factor, is greater for raw rice husk, so in the results, the sorption capacity is greater for raw rice husk. The results and calculations of the constants of all the isotherms are given below:

It is evident from the above discussion that each isotherm model was followed by the type of rice husk that had a greater value of R^2. The Langmuir isotherm is best followed by thermally treated rice husk, the Freundlich isotherm is best followed by chemically treated rice husk, and the Temkin is best followed by both raw and chemically treated rice husk [3,53]. We can also draw conclusions from the sorption capacity from the above plots. The raw rice husk had a greater sorption capacity, i.e., 14 mg/g, and for chemically and thermally treated, the values were 11 mg/g and 5 mg/g, respectively.

The adsorbents used in the present study demonstrate relatively high sorption capacities (Table 3), when comparing with other sorbents derived from waste. Ozkaya [53] performed the adsorption of phenol on commercial activated carbon and obtained a sorption capacity of 6.193 mg/g, with the Langmuir model showing better agreement with experimental data in comparison with the Redlich–Peterson and Toth models [54]. Also, Aksu and Gonen [54] observed that experimental data on the adsorption of phenol on Mowital®B30H resin-immobilized activated sludge fitted very well to the Langmuir adsorption model. Jain et al. [55] observed that sorbents prepared from waste with mainly organic constituents, such as activated carbon made of carbon slurry waste, performed better than sorbents made of waste with mainly inorganic constituents (blast furnace slag, dust, and sludge), in terms of sorption capacity of different phenolic compounds (phenol and chlorophenols). Ariyanto et al. [56] modified nanoporous carbon from coconut shell, using 30% oxygen peroxide solution and noticed that oxidation of the carbon material resulted in higher metronidazole uptake capacity. Moreover, the Langmuir model showed better fitting in comparison with the Freundlich model [56].

Table 3. Comparison of sorption capacities.

Adsorbents	Adsorbate	Sorption Capacity (mg/g)	Reference
Raw Rice Husk	resorcinol	14	Present Study
Chemically Treated Rice Husk	resorcinol	11	Present Study
Thermally Treated Rice Husk	resorcinol	5	Present Study
Commercially available activated carbon	phenol	6.19	[53]
Mowital®B30H resin immobilized activated sludge	phenol	55.6	[54]
Activated carbon slurry waste	phenol	17.2 (at 25 °C) 20.7 (at 45 °C)	[55]
	2-chlorophenol	50.3 (at 25 °C) 61.3 (at 45 °C)	
	4-chlorophenol	57.4 (at 25 °C) 69.1 (at 45 °C)	
	2,4-chlorophenol	132.5 (at 25 °C) 145.1 (at 45 °C)	
Streptomyces rimosus	methylene blue (dye)	34.3	[57]
Banana bark	rhodamine B (dye)	40.16	[58]
Mangrove bark	direct red-23 (dye)	21.55	
Pandanus leaves	malachite green (dye)	9.74	
Neem bark		0.36	
Mango bark		0.53	
Carbon xerogel modified with ethylenediamine	thymol blue	153.4	[59]
Pomegranate peel		5.28	[60]

In order to advance the efficient and sustainable treatment of wastewater, it is imperative that future research directs its attention towards investigating the adsorption capabilities of rice husks for a variety of pollutants, such as metals, dyes, phenols, and organic compounds. To assess the practicality and effectiveness of rice husks in real-world applications, pilot-plant studies should be conducted. It is crucial to develop adsorbents that possess high capacities, can be easily separated, are cost-effective, and can be recycled. Modifying rice husks specifically for heavy metals can enhance their suitability for adsorbing inorganic anions. Areas of focus for future research should include multicomponent adsorption, pilot-plant studies, studying adsorbate interactions, developing advanced adsorbents, exploring modification techniques, and evaluating uncertainties. By undertaking these research efforts, the utilization of rice husks in wastewater treatment can be advanced towards greater efficiency and sustainability.

4. Conclusions

In conclusion, this study demonstrates that rice husk can be effectively utilized as a biosorbent for the removal of resorcinol, a phenolic compound, from industrial wastewater. Due to its abundance and marginal price, such adsorbent could be attractive in comparison with commercially available alternatives. The presence of carbonyl and hydroxyl groups in all three categories of adsorbents were observed, the former likely having influence on the adsorption mechanism. XRD characterization indicated the presence of SiO_2 and Fe_3O_4 as major inorganic constituents of adsorbent materials. The removal of phenolic compounds was found to be dependent on the dose of adsorbent and the initial concentration of resorcinol. The optimized doses for RH (raw rice husk), CRH (chemically treated rice husk), and TRH (thermally treated rice husk) were found to be 0.5 g, 0.5 g, and 1.5 g, respectively. The CRH and TRH gave a maximum removal efficiency of about 80% when the effect of dose was studied. When the effect of concentration was studied, the maximum removal efficiency was found in RH, above, i.e., 90%. The sorption capacity for RH, CRH, and TRH was found to be 14 mg/g, 11 mg/g, and 5 mg/g, respectively. The Langmuir isotherm performed better than the Freundlich and Temkin isotherms in terms of the quality of fit to the experimental data.

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Appendix A

Table A1. Co-relation analysis using Heat-Map (Python Programming Software: Perkin Elmer software version 10.4.3, XRD 5.20 Mavern Paranyltical).

Co-Relation Matrix-Variables	M	Q_e	$1/q_e$	C_e/q_e	$1/C_e$	$\log(q_e)$	$\ln(C_e)$
Raw Rice Husk							
m	1	0.9642	−0.9746	0.6457	−0.6652	−0.9883	−0.9831
q_e	0.9642	1	−0.9983	0.6027	−0.6337	−0.9928	−0.9876
$1/q_e$	−0.9746	−0.9983	1	−0.5909	0.6172	0.994	0.9889
C_e/q_e	0.6457	0.627	−0.5909	1	−0.9965	−0.6346	−0.5781
$1/C_e$	−0.6652	−0.6337	0.6172	−0.9965	1	0.6402	0.5855
$\log(q_e)$	−0.9883	−0.9928	0.994	−0.6346	0.6402	1	0.9942
$\ln(C_e)$	−0.9831	−0.9876	0.9889	−0.5781	0.5855	0.9942	1
Chemically Treated Rice Husk							
M	1	0.9962	−0.999	0.6641	−0.6732	−0.9983	−0.9933
Q_e	0.9962	1	−0.9972	0.6315	−0.6554	−0.999	−0.9941
$1/q_e$	−0.999	−0.9972	1	−0.6383	0.6682	0.9974	0.9925
C_e/q_e	0.6641	0.6315	−0.6383	1	−0.9951	−0.6624	−0.5866
$1/C_e$	−0.6732	−0.6554	0.6682	−0.9951	1	0.6624	0.6247
$\log(q_e)$	−0.9983	−0.999	0.9974	−0.6224	0.6624	1	0.9947
$\ln(C_e)$	−0.9933	−0.9941	0.9925	−0.5866	0.6247	0.9947	1
Thermally Treated Rice Husk							
M	1	0.9971	−0.9949	0.6401	−0.6652	−0.996	−0.9893
Q_e	0.9971	1	−0.9953	0.6278	−0.6524	−0.998	−0.9917
$1/q_e$	−0.9949	−0.9953	1	−0.6343	0.6579	0.9954	0.9884
C_e/q_e	0.6401	0.6278	−0.6343	1	−0.9974	−0.6272	−0.5902
$1/C_e$	−0.6652	−0.6524	0.6579	−0.9974	1	0.6595	0.6218
$\log(q_e)$	−0.9966	−0.998	0.9954	−0.6272	0.6595	1	0.9921
$\ln(C_e)$	−0.9893	−0.9917	0.9884	−0.5902	0.6218	0.9921	1

Table A2. Multi-polynomial regression analysis.

Coefficients	Estimate	Std. Error	t Value	Pr(>|t|)
		Raw Rice Husk		
Intercept	0.02706	0.04325	0.626	0.581
M	0.22909	0.04095	5.595	0.021
Q_e	−0.05373	0.01138	−4.719	0.033
$1/q_e$	−0.02438	0.04391	−0.55	0.611
C_e/q_e	−0.1116	0.05321	−2.097	0.169
$1/C_e$	−0.05311	0.05734	−0.925	0.4
$\log(q_e)$	−0.11594	0.02677	−4.328	0.043
		Chemically Treated Rice Husk		
Intercept	0.0482	0.05511	0.875	0.46
M	0.19237	0.04361	4.413	0.047
Q_e	−0.06816	0.01491	−4.577	0.041
$1/q_e$	−0.05864	0.05911	−0.992	0.422
C_e/q_e	−0.06108	0.07124	−0.858	0.468
$1/C_e$	−0.05673	0.07916	−0.717	0.539
$\log(q_e)$	−0.12815	0.03683	−3.477	0.079
		Thermally Treated Rice Husk		
Coefficients	Estimate	Std. Error	t Value	Pr(>|t|)
Intercept	−0.07946	0.08486	−0.937	0.42
M	0.13906	0.0667	2.094	0.211
Q_e	−0.1607	0.02348	−6.847	0.012
$1/q_e$	0.00525	0.09154	0.057	0.955
C_e/q_e	0.02137	0.11073	0.193	0.868
$1/C_e$	−0.00233	0.12309	−0.019	0.986
$\log(q_e)$	−0.24181	0.05725	−4.224	0.052

Table A3. Effect of dose and concentration on removal efficiency.

Dose (g)		RE%	
	Raw	Chemical	Thermal
0.5	55.16526406	78.14368	46.18855958
1	46.77399683	80.77814	63.84924991
1.5	20.13660202	82.19295	76.241005
2	38.62666179	75.26528	76.28979144
Concentration (ppm)		**RE%**	
	Raw	**Chemical**	**Thermal**
1	86.61972	26.86913	76.77766
3	79.43662	52.98207	87.01061
5	83.6338	69.96707	97.89243
7	98.92019	76.58251	94.12123

Table A4. Data for isotherms.

C_p (mg/L)	C_i (mg/L)	C_i (mg/L)	C_e (mg/L)	C_e (mg/L)	$\log C_e$	C_i–C_e (mg/L)	V (L)
			Raw Rice Husk				
10	10	1	5.465839	0.54658	−0.2623	0.45342	0.1
20	20	2	12.43781	1.24378	0.09474	0.75622	0.1
30	30	3	20.84317	2.08432	0.31896	0.91568	0.1

Table A4. *Cont.*

C_p (mg/L)	C_i (mg/L)	C_i (mg/L)	C_e (mg/L)	C_e (mg/L)	log C_e	C_i–C_e (mg/L)	V (L)
Chemically Treated Rice Husk							
10	10	1	7.36	0.736	−0.13312	0.264	0.1
15	15	1.5	11.36	1.136	0.055378	0.364	0.1
25	25	2.5	19.95842	1.995842	0.300126	0.504158	0.1
Thermally Treated Rice Husk							
10	10	1	8.125	0.8125	−0.09018	0.1875	0.1
15	15	1.5	12.365	1.2365	0.092194	0.2635	0.1
25	25	2.5	20.27027	2.027027	0.30686	0.472973	0.1
30	30	3	23.654	2.3654	0.373905	0.6346	0.1

Table A5. Dosage data-treatment analysis.

M (g)	q_e	$1/q_e$	C_e/q_e	$1/C_e$	Log q_e	Ln C_e
Raw Rice Husk						
0.5	0.09068	11.0274	6.0274	1.82955	−1.04247	−0.60407
0.5	0.15124	6.61184	8.22368	0.804	−0.82032	0.218156
0.5	0.18314	5.46041	11.3812	0.47977	−0.73722	0.734441
Chemically Treated Rice Husk						
0.5	0.0528	18.93939	13.93939	1.358696	−1.27737	−0.30653
0.5	0.0728	13.73626	15.6044	0.880282	−1.13787	0.127513
0.5	0.100832	9.917526	19.79381	0.501042	−0.9964	0.691066
Thermally Treated Rice Husk						
1.5	0.0125	80	65	1.230769	−1.90309	−0.20764
1.5	0.017567	56.926	70.38899	0.808734	−1.75531	0.212285
1.5	0.031532	31.71429	64.28571	0.493333	−1.50125	0.70657
s1.5	0.042307	23.63694	55.91081	0.422761	−1.37359	0.860947

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