Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.28846

272 (2022) 220–232
October

Comparative isothermal study of phenolic removal from water using different forms of rice husk

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Received 28 March 2022; Accepted 18 August 2022

ABSTRACT

Phenolic compounds are present in human food, pharmaceuticals, dyes, antiseptics, cosmetics pesticides, and traditional medicine. Phenolic compounds are very toxic to aquatic organisms and may cause tissue erosion, paralysis of the central nervous system, denaturing of protein, and damage to the kidney, liver, and pancreas. These compounds are toxic even at extremely low concentrations hence treatment is required. In this study resorcinol, phenyl diamine, and 2-naphthol were treated using different forms of rice husk, that is, raw rice husk powder thermally treated rice husk powder and chemically treated rice husk powder. The characterization of these adsorbents showed the existence of C=O and OH functional groups and silica as a major component. The method was developed by using a standard solution of phenolic compounds having a limit of detection (2.9–7.89 ppm) and a limit of quantification (2.3–8.7). Optimization of parameters showed that an adsorbent dose of 20 g gave maximum removal efficiency for phenolic compounds (80%). The initial concentration of phenols was optimized at 40 ppm. Langmuir isotherm showed thermal treated and raw rice husk powder followed uni-layer model while Freundlich and Temkin isotherms showed mixed affinity of adsorbents with phenols under study. The overall adsorption of phenols was a physical endothermic process as suggested by Dubinin–Radushkevich and Flory–Huggins isotherms.

Keywords: Rice husk; Adsorption; Phenolic compounds; Isotherms

1. Introduction

Water contains many impurities like acids, salts, dyes, toxic chemicals, and trace elements [1] and phenolic compounds are one of them. These compounds pollute water and wastewater in direct and indirect ways. Phenols are considered priority pollutants as their minute quantity (0.002 mg/L) can create problems for living organisms. High solubility in water, toxicity, and mutagenic characteristics of phenols make them extremely dangerous (both synthetic and natural phenols). Problems like vertigo, CNS disturbance, confusion, liver and kidney damage, vomiting, diarrhea, asthma, nausea, and systematic injury are common effects of phenolic compounds present in drinking water. Phenols can enter the environment through various sources, that is, paint, pesticide, coal conversion, polymeric resin, petroleum, wood treatment process plants, and the dyes industry. Phenolic compounds, when discharged into the environment, are responsible for the deterioration of drinking water quality. Different compounds such as 2-naphthol, resorcinol, and *p*-phenylenediamine are the most applied organics in the industrial sector.

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These compounds are poor biodegradable compounds, therefore, when these are discharged into the environment, it is necessary to treat the water. Various treatment processes like membrane-based extraction [2], cross linked cyclo dextrin particles ozonation [3], electrochemical oxidation [4], distillation [5], advanced oxidation [6], photolytic degradation [7], and adsorption [8] have been used for the removal of phenols from water. However, these techniques possess certain drawbacks as the common disadvantage of the membrane-based extraction method is the constant resistance linked to the membrane itself, which results in reduced water flux rates. Ozonation, on the other hand, generates toxic by-products and cannot complete the mineralization of water pollutants. Electrochemical oxidation is highly dependent on electricity and there is a constant need for the replacement of electrodes [8], whereas the distillation process requires high energy and large space (for a distillation tower) [9]. Although advanced oxidation processes are considered very efficient in phenol removal, they are expensive, owing to the usage of electrical energy when ultraviolet is applied [9]. Moreover, during photolytic degradation, various intermediates are produced which are considered more hazardous than the original materials [10]. Among these methods, adsorption is considered a quite simple, efficient, and inexpensive treatment method, compared to other techniques [11,12]. The frequently used adsorbents for the elimination of phenols from water include chitosan [13], activated carbon [14], sawdust [15] agricultural wastes [16], and clay [17], but many problems are related to these traditional adsorbents for example poor yield [18], expensive to synthesize [19], and poor sorption selectivity [20].

Recently, people are focusing on the use of adsorption for the removal of phenols [21]. Various adsorbents, that is, nickel oxide nanoparticles [22], chitosan-based nanoparticles [23], and carbon nanotubes [24] were used for the treatment of phenolic compounds from drinking water. These techniques gave reliable results but are expensive. The preparation of nanoparticles needs expertise and is not cost effective. A bulk quantity of adsorbent is required to increase the surface area and pore sites of the adsorbent for better removal efficiency. This leads researchers to use agricultural waste as an adsorbent. Rice husk is a waste that is abundantly produced. In this research work three forms of rice husk, that is, raw, chemically treated, and thermally treated, were studied for the elimination of phenolic compounds. This research aims to compare the removal efficiency of adsorbents (waste as adsorbent) and adsorption isotherms to suggest a more efficient treatment for the removal of phenolic compounds.

2. Experimental

2.1. Method validation

To evaluate the defining property of the material against already established standards, an analytical method has been developed. The distinguishing factors that may be analyzed during method development include linearity, limit of quantification (LOQ), limit of detection (LOD), range, precision, and accuracy [25]. For validation of the analytical method, the guidelines established by the ICH (International Conference on the Harmonization of Technical Requirements for the Registration of Pharmaceuticals for Human Use) were followed. For the development of the analytical method, standard solutions of phenols (10–40 ppm) were prepared, and three calibration curves were formed using high-performance liquid chromatography (HPLC, Hitachi). The mobile phase was acetonitrile and a flow rate of 1 mL was selected. the column used for this procedure was C18. The values of λ_{max} used for the calibration curve were 273 nm for resorcinol, 453 nm for *p*-phenylenediamine, and 273 nm for 2-naphthol. Every concentration was examined on HPLC (Fig. 1) in triplicate and the average of it was used for the calibration curve (Fig. 2) and method validation. The validation characteristics (Tables 1 and 2) like slope, intercept, R^2 (coefficient of regression), LOD, LOQ, STD (standard deviation), and %RSD (%age relative standard deviation) were determined. Following mathematical relationships were used for the calculation of various parameters.

$$\mathrm{SD} = \sqrt{\frac{\sum(x-\bar{x})^2}{N}} \tag{1}$$

where N = number of data points; x = value of data point; $\bar{x}$ = mean value of data point.

$$\%\mathrm{RSD} = \left(\frac{\mathrm{STD}}{\bar{x}}\right)\times 100 \tag{2}$$

$$\mathrm{LOD} = \frac{3.3\times \mathrm{STD}}{\mathrm{Slop}} \tag{3}$$

$$\mathrm{LOQ} = \frac{10\times \mathrm{STD}}{\mathrm{Slop}} \tag{4}$$

Using these mathematical relations, the lowest standard deviation was observed in the case of *p*-phenylamine (3.68) while a high LOD value was observed for resorcinol (29.01) and the highest LOQ was observed for resorcinol (87.91). The R^2 values were close to 1 which indicated that the relationship (Fig. 2) is obeying Beer–Lambert law [26].

2.2. Preparation of adsorbents

All chemicals were analytical grade and purchased from Merck, Pakistan. Rice husk was purchased from the local market. It was washed with distilled water (3 times) and dried in sunlight for 72 h. After drying, the husk was ground into powder form. The mesh size of the husk was obtained using a 1.41 mm sieve (USA standard testing sieve, No 14, Fisher Scientific Company). The elemental composition of rice husk powder is given in (Table 3). The rice husk powder was then divided into three portions for further process, that is, raw rice husk powder (RRHP), chemically treated rice husk powder (CRHP), and thermally treated rice husk powder (TRHP). For RRHP, the rice husk powder was used without any treatment. For CRHP, 200 g of rice husk powder was treated with 0.1 M HNO_3 followed by soaking in methanol. It was used after drying at 103°C ± 2°C for 45 min. for

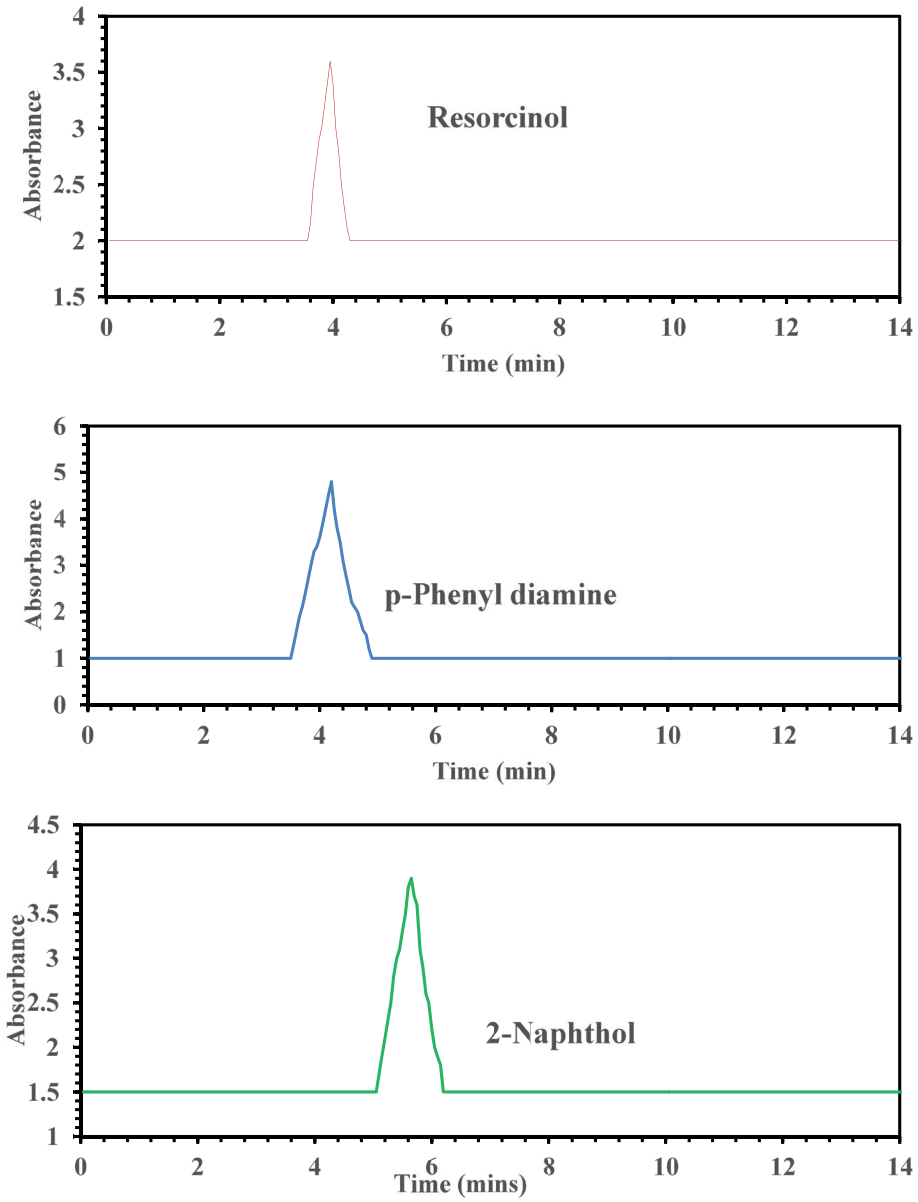

Fig. 1. HPLC chromatogram of resorcinol, *p*-phenylenediamine, and 2-naphthol used in the study.

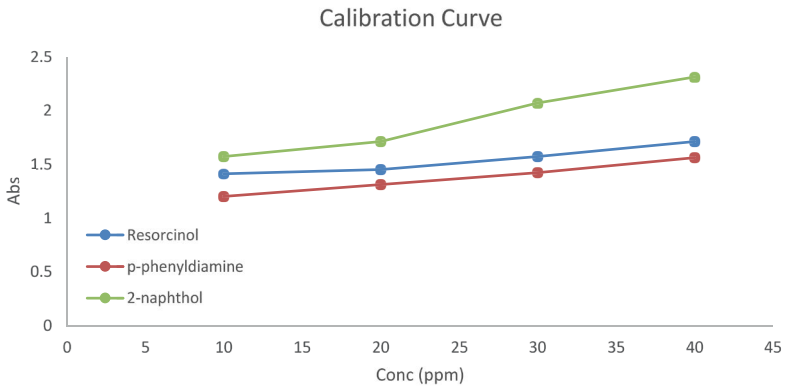

Fig. 2. Calibration curve of standard phenolic compounds for the method validation.

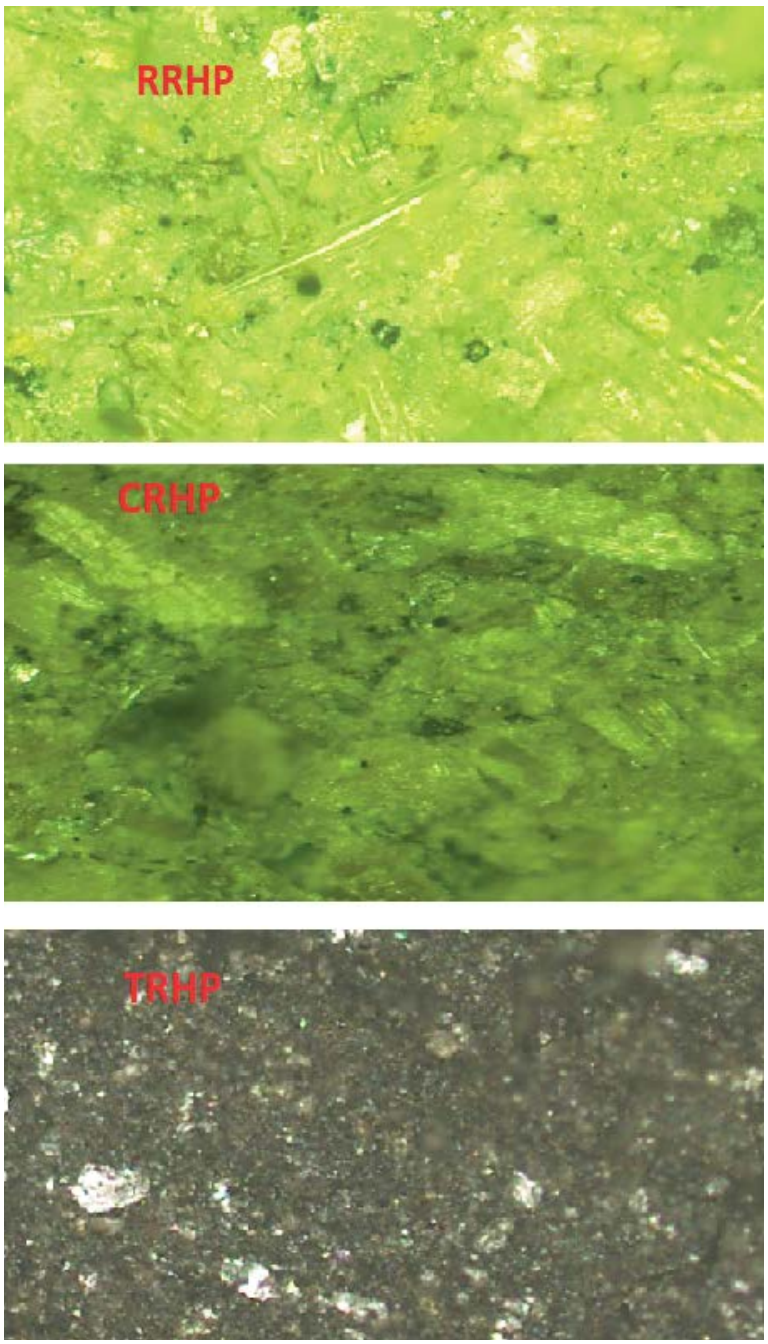

Fig. 3. Laser microscopic images (STM7, reflective mode) of different adsorbents used in the study.

TRHP, 100 g powder of rice husk was heated at 400°C in a muffle furnace and used after cooling. The characterization of these three adsorbents was performed using laser microscopy, Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) analysis. To study the adsorption mechanism various isotherms were also studied.

2.3. Optimization of adsorption parameters

For optimization of adsorption, two parameters, that is, the dose of adsorbent (g/L) and initial concentration (ppm) of phenolic compounds were used. Adsorbent doses of 5–20 g/L were selected while the 10–40 ppm concentration of phenols was used. 100 mL of the prepared solution was added with a selected dose of adsorbent and then agitated for 60 min at 100 rpm. After that, the solution was filtered, and the filtrate was used for the estimation of the remaining phenolic compound using HPLC (method details are given in the previous section). The removal efficiency vs dose of adsorbent and initial concentration of phenolic compounds were plotted (Figs. 6 and 7) and optimum conditions were selected.

Table 1
Concentration and recovery calculation using the calibration curve of phenolic compounds used in the study

Prepared conc.	Exp. conc.	Recovery %
	Resorcinol	
10	12.75	127.45
20	16.67	83.33
30	28.43	94.77
40	42.16	105.39
	p-phenylenediamine	
10	10.50	105.04
20	19.75	98.74
30	28.99	96.64
40	40.76	101.89
	2-naphthol	
10	11.63	116.28
20	17.05	85.27
30	31.01	103.36
40	40.31	100.78

Table 2
Measure parameters for the method validation using standard phenolic compounds used in the study

	Resorcinol	*p*-phenylenediamine	2-naphthol
Std. Dev.	18.78	3.68	12.72
SE of intercept	0.04	0.01	0.08
SD of intercept	0.09	0.03	0.16
LOD	2.9	7.89	2.16
LOQ	8.7	2.3	6.1
R	0.98	1.00	0.99
RSD%	18.28	3.66	12.55
Slope	0.01	0.01	0.03
Intercept	1.28	1.08	1.27
R^2	0.95	1.00	0.98

3. Results and discussion

3.1. Characterization of adsorbents

The elemental composition of rice husk powder (RHP) was determined (Table 1). The results indicated that rice husk contains an abundance of silicates which is a good adsorbent. The adsorbents were characterized using FTIR, XRD, and laser microscopy. The images (Fig. 3) obtained by laser microscopy STM7 (reflective mode) showed not much variation for RRHP and CRHP while TRHP showed an appearance of charcoal as the TRHP samples were obtained after heating at 400°C. The FTIR spectra were used for the presence of different functional groups. Fig. 4 shows the FTIR response of adsorbents from 4,000–400 cm^{-1} (wavenumber). The three forms of rice husk showed a broad peak between 3,700–3,600 cm^{-1} indicating the presence of –OH (hydroxyl) group; at 1,650–1,600 cm^{-1} indicated –C=O (carbonyl); at 1,050–1,040 cm^{-1} indicated –C–O–C– (ether linkage) [27]. The XRD pattern of adsorbents are shown in Fig. 5. Characteristics peaks of SiO_2 at 27°, 42°, and 50° were present in RRHP, CRHP, and TRHP [28].

Table 3
Elemental composition of adsorbent used in the study

Rice husk	wt.%
Si	44.20
S	0.07
Mg	0.11
Ca	0.15
Na	0.04
K	0.38
O	50.93

3.2. Optimization of adsorption parameters

After method validation, optimization of adsorption parameters (concentration and dose) has been performed. For this purpose, standard solutions of 10, 20, 30, and 40 ppm were prepared. Adsorbent doses of 5, 10, 15, and 20 g/L were used. For resorcinol, maximum removal efficiency (RE%) was observed with CRHP (>80%) while minimum RE% was observed with RRHP (20%–40%). No major effect of dose variation was observed in the case of CRHP as the same RE% was observed at all dose amounts. TRHP gave good RE% at higher dose values, that is, 20 g/L and it is the same as CRHP. The RE% of RRHP was increased with an increase in dose amount. An amount of 20 g/L gave maximum RE% for all the adsorbents for resorcinol removal (Fig. 6). For *p*-phenylamine, CRHP gave maximum RE% (up to 75%) while RRHP gave a minimum of 10% RE. The values of RE% decreased with an increase in dose, for RRHP, which may be due to stearic effects on active sites of RRHP for phenolic removal [29]. The TRHP showed an increase in RE% with the increase in dose amount. An amount of 5 g/L gave maximum RE% for all adsorbents for *p*-phenylamine. For 2-naphthol, CRHP gave maximum RE%, that is, 60% while RRHP gave minimum RE% (25%–40%). The RE% values for TRHP increase with an increase in dose amount. A dose of 20 g/L gave maximum RE% for all the adsorbents for 2-naphthol. This suggests that the active sites which are available for phenol adsorption are enough for the removal of phenol concentration [29].

3.2.1. Effect of concentration

Various concentrations of phenolic solution (10–40 ppm) were subject to a fixed dose of adsorbent (20 g/L) to study the effect of concentration on RE%. For resorcinol, all adsorbents were showing an increase in RE% as the increase in the concentration (Fig. 7). This suggested that the active sites available on the adsorbent surface can easily adsorb phenolic compounds. The maximum RE% was observed in the case of RRHP and TRHP (<95%) while CRHP showed minimum RE% even at high concentrations, that is, 40 ppm

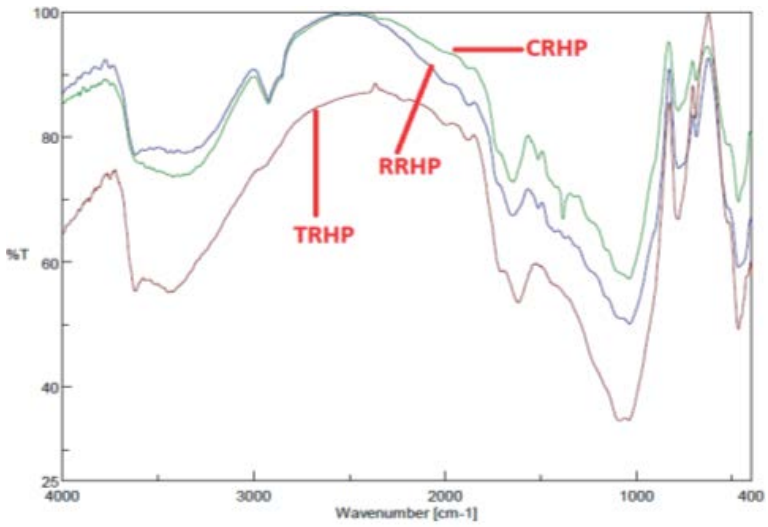

Fig. 4. FTIR of different adsorbents used in the study for identification of functional groups.

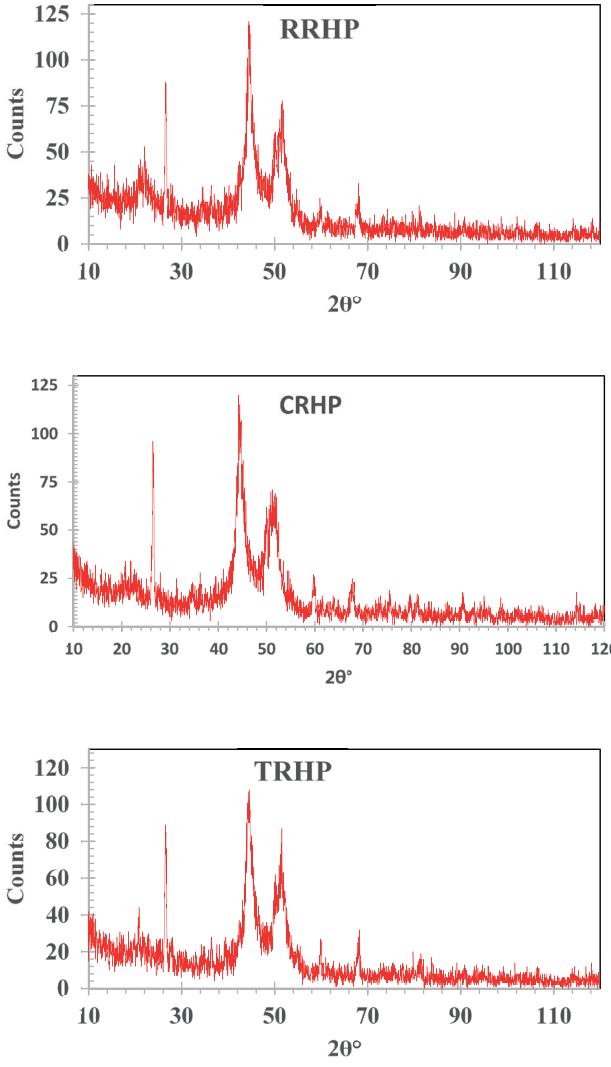

Fig. 5. XRD pattern of various adsorbents used in the study.

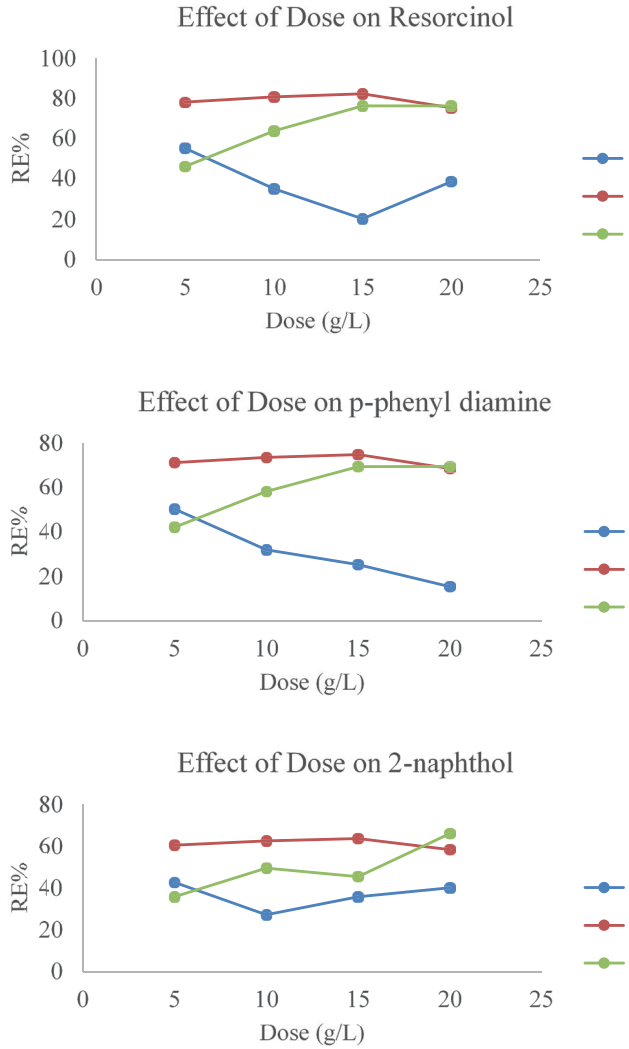

Fig. 6. Effect of adsorbent dose on the removal of phenolic compounds from water.

Table 4
Mathematical models/equations for various isotherms used in the study

S. No.	Isotherm	Mathematical equation		Reference
1.	Langmuir	$\frac{C_e}{q_e}=\frac{C_e}{q_m}+\frac{1}{q_m\times b}$	(5)	[31]
2.	Freundlich	$\log q_e=\log K_f+\frac{1}{n}\log C_e$	(6)	
3.	Temkin	$q_e=\beta\ln\alpha+\beta\ln C_e$	(7)	
4.	Dubinin–Radushkevich	$\ln q_e=\ln\left(q_s\right)-\left(K_{\text{ad}}\varepsilon^2\right)$	(8)	
5.	Flory–Huggins	$\log\frac{\theta}{C_o}=\log K_{\text{FH}}+n\cdot\log\left(1-\theta\right)$	(9)	

Equation (1): C_e: equilibrium concentration of adsorbate (mg/L); q_e: the amount of metal adsorbed per gram of adsorbate at equilibrium; q_m: maximum monolayer coverage capacity (mg/g); b: Langmuir Langmuir isotherm constant.
Equation (2): K_f: Freundlich isotherm constant; n: adsorption intensity.
Equation (3): β: Temkin constant.
Equation (4): q_s: theoretical isotherm saturation capacity; K_{ad}: Dubinin–Radushkevich isotherm constant; ε: Dubinin–Radushkevich.
Equation (5): θ: degree of surface coverage; n: number of ions occupying adsorption sites; K_{FH}: Flory–Huggins isotherm constant.

of resorcinol solution. For *p*-phenylamine, the response was like resorcinol, that is, an increase in concentration increases the RE% which was due to the abundance of active sites on adsorbents. The maximum RE% was given by TRHP (<80%). For 2-naphthol, no clear pattern was observed in all adsorbents although, at 40 ppm concentration, maximum RE% was achieved, that is, 80% which is due to common –OH interaction [30]. The minimum RE% was observed in the case of CRHP, that is, >50%.

3.3. Isotherm study

Various isotherms, that is, Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, and Flory–Huggins were studied (Table 4) for the removal of phenolic compounds using different adsorbents. The tentative mechanism of adsorption was also studied. Different concentrations of phenolic compounds (40–60 ppm) at pH 8 were introduced with 20 g/L of adsorbent dose.

3.3.1. Langmuir isotherm

The mathematical model of the Langmuir isotherm is given in Table 4 (Eq. 1). The plot (Fig. 8) of C_e/q_e vs. C_e was used for determining the values of b and q_m. The values of parameters obtained using the Langmuir isotherm are given in Table 5. For resorcinol, the values of R^2 were close to 1.0 except in the case of TRHP (0.52) which suggested that adsorption of resorcinol can be well defined in the case of RRHP and CRHP, but TRHP does not follow the Langmuir model. The values of q_m were in order of RRHP > TRHP > CRHP which showed RRHP has maximum adsorption capacity for resorcinol. The Langmuir constant (b) was maximum in the case of RRHP indicating a good affinity for resorcinol while other adsorbents have a poor affinity [31] for resorcinol (Table 5). For *p*-phenylamine, R^2 response was similar to resorcinol, that is, except TRHP, all other adsorbents were following the Langmuir model (Table 5) as values were close to 1. The maximum adsorption capacity (q_m) was observed in the case of RRHP (2.8 mg/g) while the minimum was observed for CRHP (0.26 mg/g). The Langmuir constant (b) of *p*-phenylamine with adsorbents was in the order of RRHP > CRHP > TRHP. 2-naphthol adsorption by RRHP and CRHP can be explained by the Langmuir model as values are closer to 1 whereas TRHP does not obey this model. Langmuir constant values were in order of TRHP > RRHP > CRHP.

3.3.2. Freundlich isotherm

The mathematical model of the Freundlich isotherm is given in Table 4 (Eq. 2). A plot (Fig. 9) of $\log q_e$ vs. $\log C_e$ was used to estimate the values of K_f and n, which are Freundlich constants depicting adsorption capacity and adsorption intensity, respectively. K_f reflects the feature of adsorbent dosage, adsorbate, and temperature, whereas, n is a non-linear factor related to the properties of the adsorption system, indicating heterogeneous energy of the adsorption surface [32]. The values of various parameters obtained from the Freundlich isotherm are presented in Table 6. For resorcinol, the table depicts that the coefficient of correlation (R^2) values for RRHP, CRHP, and TRHP are quite closer to 1. Moreover, n values for both RRHP and CRHP are 1.87 and 1.55 (greater than 1) whereas, for TRHP, it is less than 1, which confirms that the Freundlich model is favorable for RRHP and CRHP. Similarly, for *p*-phenylamine, the values of R^2 are closer to unity in the case of RRHP and CRHP, however, TRHP shows less R^2 value (0.91). In addition, only RRHP shows n value greater than 1, that is, 2.78, which means that the Freundlich model is favorable for

Table 5
Various parameters calculated using Langmuir isotherm for the removal of phenolic compounds using different adsorbents under study

Parameters	RRHP	CRHP	TRHP
	Resorcinol		
Slope	1.05	1.40	1.21
Intercept	12.11	31.25	147.23
q_m	0.95	0.71	0.83
R^2	1.00	1.00	0.52
B	0.09	0.04	0.01
R_L	0.32	0.24	0.88
	p-phenylenediamine		
Slope	0.36	3.88	0.50
Intercept	0.96	25.06	17.85
q_m	2.80	0.26	2.02
R^2	0.98	0.94	0.62
B	0.37	0.15	0.03
R_L	0.10	0.08	0.68
	2-naphthol		
Slope	1.66	3.49	0.42
Intercept	3.73	8.63	1.90
q_m	0.60	0.29	0.93
R^2	0.99	0.97	0.62
B	0.45	0.40	0.57
R_L	0.08	0.03	0.09

Table 6
Various parameters calculated using the Freundlich model for the removal of phenolic compounds using different adsorbents

Parameters	RRHP	CRHP	TRHP
	Resorcinol		
Slope	0.53	0.65	1.12
Intercept	0.37	0.66	2.13
n	1.87	1.55	0.89
K_f	2.35	4.59	133.75
R^2	0.98	1.00	0.98
	p-phenylenediamine		
Slope	0.36	2.94	2.04
Intercept	0.36	0.10	1.19
n	2.78	0.34	0.49
K_f	2.27	1.25	15.34
R^2	0.99	0.98	0.91
	2-naphthol		
Slope	0.22	0.65	0.50
Intercept	0.10	0.09	0.31
n	4.52	1.53	1.98
K_f	1.26	1.24	2.06
R^2	0.90	0.97	0.91

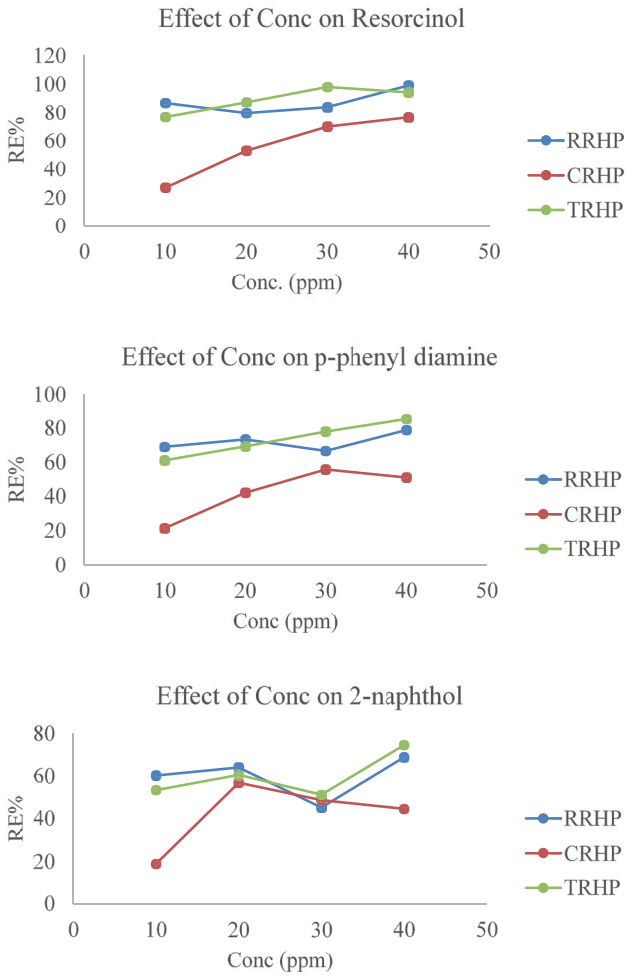

Fig. 7. Effect of phenol concentration on removal efficiency using different adsorbents.

only RRHP. In the case of 2-naphthol, although n values are greater than 1 for all types of rice husk materials (RRHP, CRHP, and TRHP), only CRHP shows a high R^2 value (0.97) which means that only CRHP obeys Freundlich isotherm.

3.3.3. Temkin isotherm

Table 4 (Eq. 3) presents a mathematical model for Temkin isotherm whereas Fig. 10 displays the plot between the quantity sorbed (q_e) and $\ln C_e$. The Temkin constants a and b can be calculated from the slope and intercept of the linear plot. Correlation coefficient (R^2) values for resorcinol indicate that RRHP and CRHP strongly follow the Temkin model (Table 7). In the case of the adsorption process of *p*-phenylamine onto different types of rice husk materials, it can be observed that the sorption process moderately follows Temkin isotherm. For 2-naphthol, Temkin isotherm favorably fits for both CRHP and TRHP due to larger R^2 values, that is, 0.98 for both materials. High correlation coefficients also depict that the adsorption process of various phenols onto rice husk materials follows the chemisorption phenomenon with physical forces [32].

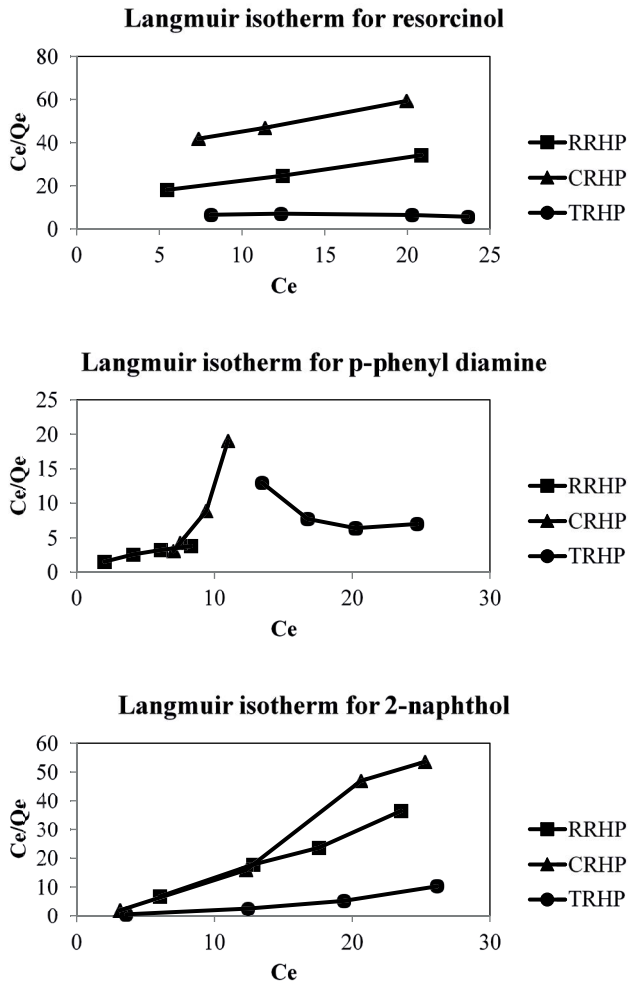

Fig. 8. Langmuir isotherm for removal of phenolic compounds using different adsorbents under study.

3.3.4. Dubinin–Radushkevich isotherm

The mathematical model of the Dubinin–Radushkevich isotherm is presented in Table 4 (Eq. 4). The plot (Fig. 11) of $\ln q_e$ vs. ε^2 results in a straight line, and its slope is equal to K_{ad}. Thus, the mean biosorption energy (E) can be calculated using the following equation.

$$E = \frac{1}{\sqrt{-2 \times \text{slope}}} \tag{10}$$

The E value is used to evaluate the type of ongoing adsorption phenomenon [31]. If the value of E is between 8 and 16 kJ/mol, then it is assumed that the process of adsorption is chemical sorption. On the other hand, if values are lower than 8 kJ/mol then it indicates that the adsorption process is physical adsorption. In this study, the E values have been presented in Table 8 and ranged between 0.09 to 0.354 kJ/mol, which indicates the adsorption of phenolic compounds onto all types of rice husk materials, that is, RRHP, CRHP, and TRHP, occurs through a physical process. In addition, keeping in view the correlation values (R^2), it can be assumed that sorption of resorcinol onto RRHP and CRHP strongly fits Dubinin–Radushkevich isotherm whereas, for *p*-phenylamine, Dubinin–Radushkevich isotherm is only favorable in the case of TRHP. Similarly, due to poor R^2 values, the adsorption phenomenon of 2-naphthol onto all types of rice husk materials does not follow the Dubinin–Radushkevich isotherm.

Table 7
Various parameters calculated using Temkin isotherm for the removal of phenolic compounds using different adsorbents under study

Parameters	RRHP	CRHP	TRHP
Resorcinol			
Slope	0.23	0.16	0.01
Intercept	0.09	0.15	0.02
R^2	1	1	0.92
α	13.9	3.01	1.79
β	0.09	0.15	0.02
p-phenylenediamine			
Slope	0.6	3.63	0.42
Intercept	0.83	9.23	0.98
R^2	0.96	0.97	0.96
A	2.07	1.48	1.54
B	0.83	9.23	0.98
2-naphthol			
Slope	0.17	0.62	0.25
Intercept	1.2	2.38	1.09
R^2	0.93	0.98	0.98
A	1.15	1.3	1.25
B	1.2	2.38	1.09

3.3.5. Flory–Huggins isotherm

Flory–Huggins isotherm model was employed to evaluate the feasibility and spontaneous nature of the adsorption process occurring between phenolic compounds and different rice husk materials (RRHP, CRHP, and TRHP). The mathematical model of Flory–Huggins isotherm is given in Table 4 (Eq. 5). The plot (Fig. 12) of $\log(\theta/C_0)$ vs. $\log(1-\theta)$ for the adsorption process was established (Fig. 6) and regression lines were obtained. Values of R^2 for the resorcinol sorption onto RRHP and CRHP depict that this isotherm strongly fits the adsorption process for both materials (Table 9). However, in the case of *p*-phenylamine, this isotherm is only suitable for RRHP (R^2 = 0.97). Moreover, the Flory–Huggins isotherm model poorly fits the adsorption phenomenon of 2-naphthol onto all types of understudied rice husk materials due to lower R^2 values. The value of K_{FH} was used for the calculation of spontaneity free Gibbs energy. The Gibbs free energy of spontaneity is related to the equilibrium constant as follows,

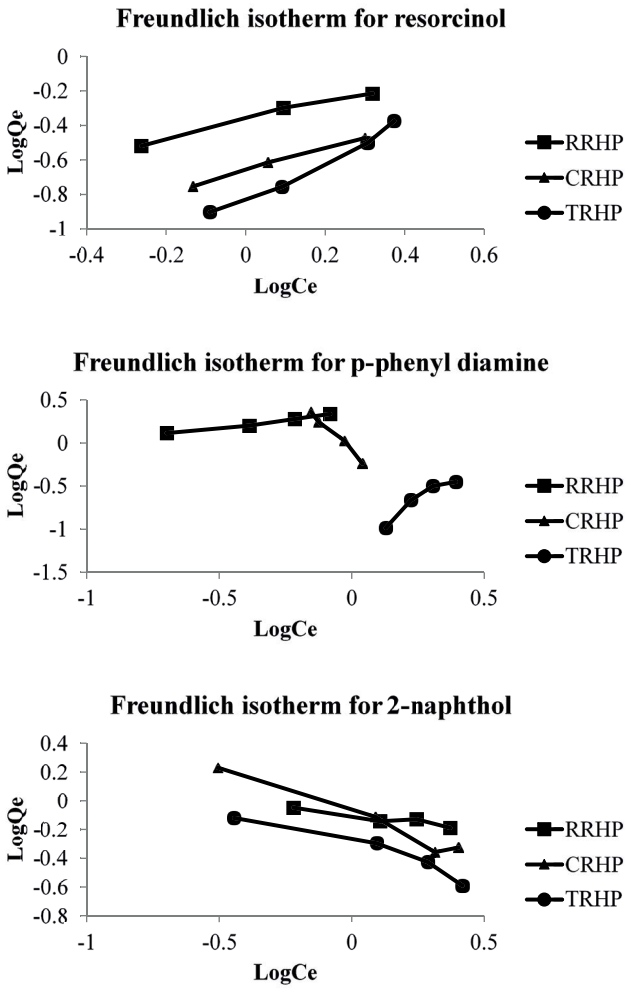

Fig. 9. Freundlich isotherm for the removal of phenolic compounds using different adsorbents used in the study.

$$\Delta G^{o} = -RT\ln K_{FH} \quad (11)$$

where R is the universal gas constant 8.324 J/mol, T is the absolute temperature (K) and K_{FH} is an equilibrium constant from the Flory–Huggins isotherm equation. $\Delta G°$ value was found positive for all types of phenols, indicating that the reaction was endothermic in nature.

4. Conclusion

Various phenolic compounds were treated using different forms of rice husk. The results showed that the method was valid with good accuracy and precision. The characterization of different adsorbents showed the abundance of silica (elemental analysis). The FTIR showed –OH, and –C=O functional groups were present in the adsorbent while XRD confirmed the presence of Silica due to its characteristic peaks. An adsorbent dose of 20 g gave maximum RE% for resorcinol and phenyl diamine (up to 80%) while for 2-naphthol it was 60%. 40 ppm of initial concentration gave maximum (80%) RE% for phenyl diamine and

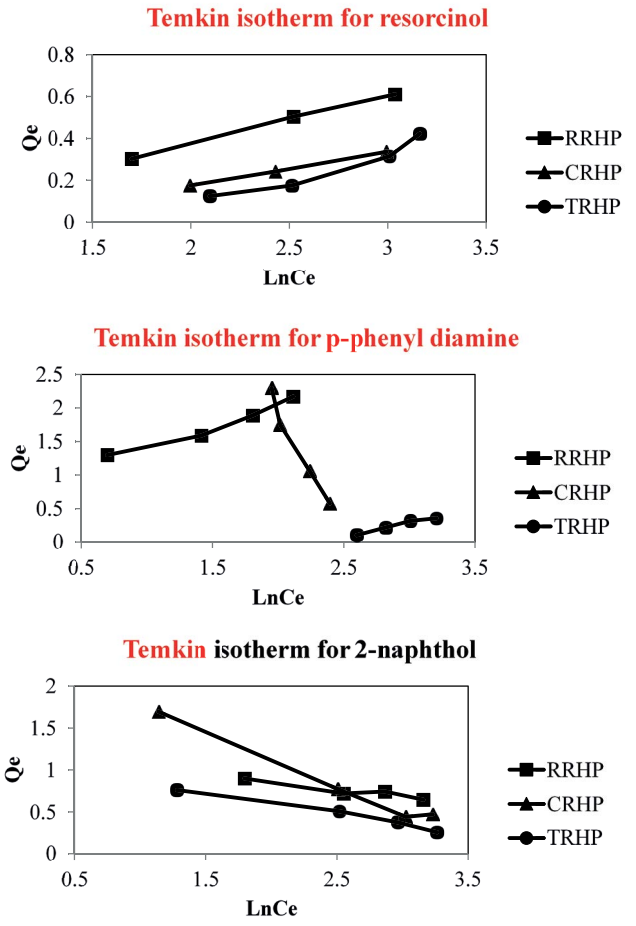

Fig. 10. Temkin isotherm for removal of phenolic compounds using different adsorbents under study.

2-naphthol while for resorcinol, 40% removal efficiency was observed. isothermal data were obtained for three phenolic compounds, following results have been obtained.

- Langmuir isotherm best fits RRHP and CRHP for resorcinol. For phenyl diamine, RRHP showed the best fit model for Langmuir while TRHP has the least affinity. 2-naphthol had a good affinity with TRHP and the least affinity with CRHP.
- Freundlich isotherm favors RRHP and CRHP for resorcinol. For phenyl diamine, only RRHP showed good affinity while poor affinity was observed in TRHP and CRHP. For 2-naphthol, CRHP showed good affinity while RRHP and TRHP showed poor affinity.
- Temkin isotherms best fit for RRHP and CRHP while TRHP showed poor results. For phenyl diamine, all three adsorbents showed good affinity. For 2-naphthol CRHP and TRHP showed good affinity while RRHP showed less affinity.
- Dubinin–Radushkevich isotherm showed a physical adsorption process for RRHP and CRHP. For phenyl diamine, TRHP showed a physical adsorption process. 2-naphthol showed that adsorption was the physical process by all three adsorbents.

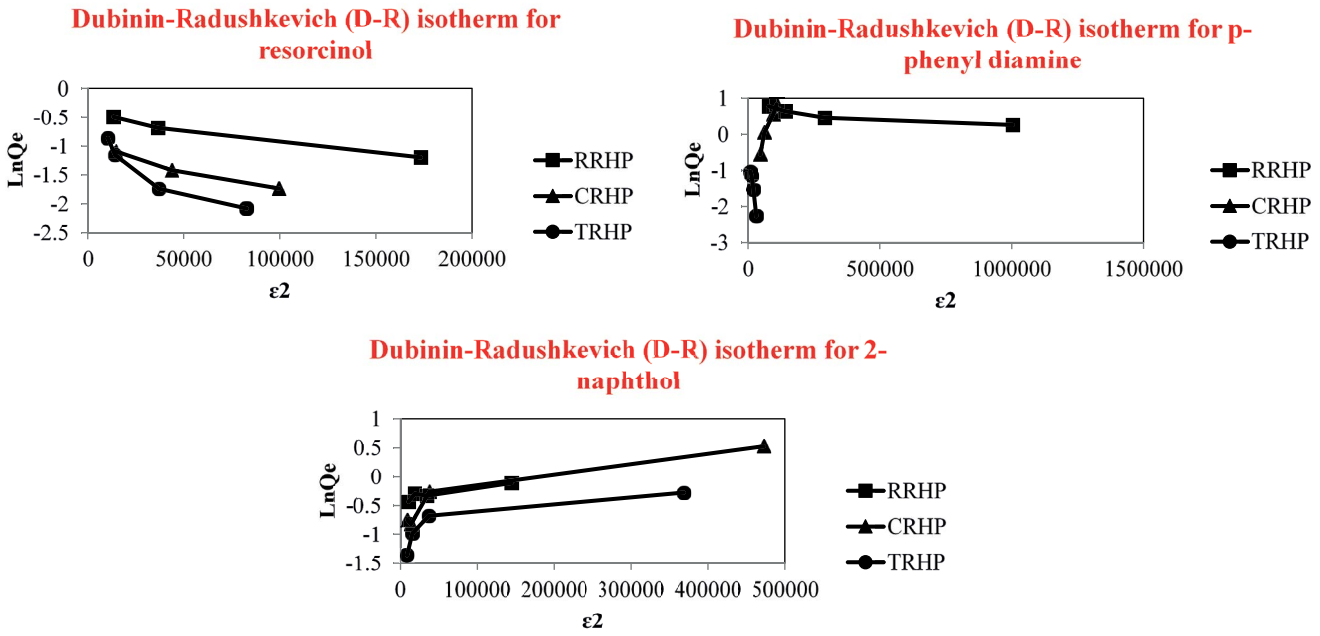

Fig. 11. Dubinin–Radushkevich isotherm for removal of phenolic compounds using different adsorbents under study.

Table 8
Various parameters calculated using Dubinin–Radushkevich isotherm for the removal of phenolic compounds using different adsorbents under study

Parameters	RRHP	CRHP	TRHP
Resorcinol			
Slope	4	0.7	20
Intercept	0.48	1.03	3.89
K	4	7	2
q_m	1.62	2.79	49
E	0.354	0.27	0.16
R^2	0.98	0.97	0.87
p-phenylenediamine			
Slope	50	2000	6000
Intercept	0.71	1.41	0.39
K	0.5	20	60
q_m	2.05	4.09	1.48
E	1	0.16	0.09
R^2	0.84	0.96	0.98
2-naphthol			
Slope	200	300	200
Intercept	0.4	0.67	1.06
K	2	3	2
q_m	1.49	1.95	2.89
E	0.5	0.4	0.5
R^2	0.86	0.87	0.69

Table 9
Various parameters calculated using Flory–Huggins isotherm for the removal of phenolic compounds using different adsorbents under study

Parameters	RRHP	CRHP	TRHP
Resorcinol			
Slope	6.24	14.41	13.55
Intercept	6.89	8.08	1.69
R^2	1	1	0.31
N	4.87	4.72	4.63
K_{FH}	97×10^5	33×10^5	54×10^3
ΔG	15.63	18.34	3.84
p-phenylenediamine			
Slope	1.17	0.31	0.18
Intercept	5.16	4.02	4.98
R^2	0.97	0.61	0.03
N	4.87	4.72	4.63
K_{FH}	17×10^5	55×10^5	14×10^5
ΔG	11.72	9.11	11.3
2-naphthol			
Slope	2.38	1.5	1.68
Intercept	5.31	5.18	5.24
R^2	0.93	0.89	0.86
N	4.87	4.72	4.63
K_{FH}	20×10^5	17×10^5	18×10^5
ΔG	12.06	11.76	11.9

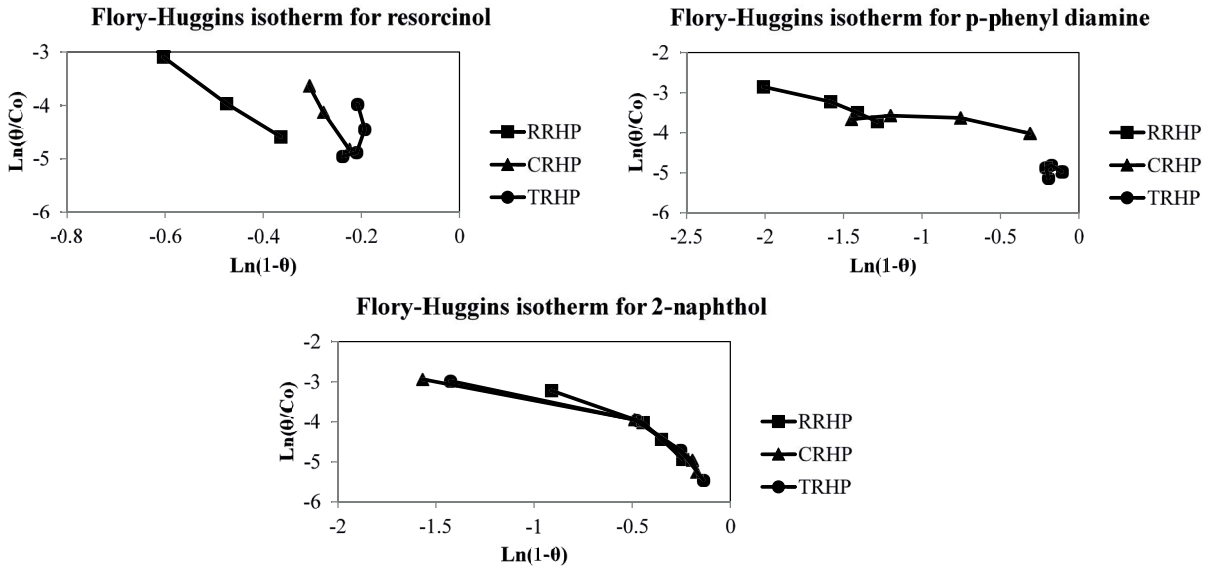

Fig. 12. Flory–Huggins isotherm for removal of phenolic compounds using different adsorbents under study.

- In Flory–Huggins isotherm, resorcinol showed endothermic adsorption for RRHP and CRHP. For phenyl diamine, RRHP showed an endothermic adsorption process while for 2-naphthol all three adsorbents showed an endothermic adsorption process.

Ethics approval and consent to participate

NA

Consent for publication

NA

Availability of data and materials

Can be provided on the request.

Competing interests

Authors have no competing interest whatsoever.

Funding

NA

Authors' contributions

Muhammad Irfan Jalees: Original Idea and manuscript writing; Azka Javed & Nayab Zahara: experimental work; Arfa Iqbal: isotherm data interpretation; Madeeha Batool: interpretation of HPLC results.

Acknowledgement

The authors are thankful to the Pakistan Council of Scientific and Industrial Research (PCSIR) Laboratories, Lahore for providing analytical facilities.

References

[1] A. Iqbal, M.I. Jalees, M.U. Farooq, E. Cevik, N.D. Mu'azu, Synthesis and application of maghemite nanoparticles for water treatment: response surface method, Desal. Water Treat., 244 (2021) 212–225.
[2] L.G.C. Villegas, N. Mashhadi, M. Chen, D. Mukherjee, K.E. Taylor, N. Biswas, A short review of techniques for phenol removal from wastewater, Curr. Pollut. Rep., 2 (2016) 157–167.
[3] H. Guo, X. Li, G. Li, Y. Liu, P. Rao, Preparation of SnO_x-MnO_x@Al_2O_3 for catalytic ozonation of phenol in hypersaline wastewater, Ozone: Sci. Eng., (2022) 1–14, doi: 10.1080/01919512.2022.2084031.
[4] L. Seid, D. Lakhdari, M. Berkani, O. Belgherbi, D. Chouder, Y. Vasseghian, N. Lakhdari, High-efficiency electrochemical degradation of phenol in aqueous solutions using Ni-PPy and Cu-PPy composite materials, J. Hazard. Mater., 423 (2022) 126986, doi: 10.1016/j.jhazmat.2021.126986.
[5] C. Eryılmaz, A. Genç, Review of treatment technologies for the removal of phenol from wastewaters, J. Water Chem. Technol., 43 (2021) 145–154.
[6] W.F. Elmobarak, B.H. Hameed, F. Almomani, A.Z. Abdullah, A review on the treatment of petroleum refinery wastewater using advanced oxidation processes, Catalysts, 11 (2021) 782, doi: 10.3390/catal11070782.
[7] X. He, H. Chi, M. He, B. Zhang, J. Zhang, D. Wang, J. Ma, Efficient removal of halogenated phenols by vacuum-UV system through combined photolysis and OH oxidation: efficiency, mechanism and economic analysis, J. Hazard. Mater., 403 (2021) 123286, doi: 10.1016/j.jhazmat.2020.123286.
[8] Y. Dehmani, D. Dridi, T. Lamhasni, S. Abouarnadasse, R. Chtourou, E. Lima, Review of phenol adsorption on transition metal oxides and other adsorbents, J. Water Process Eng., 49 (2022) 102965, doi: 10.1016/j.jwpe.2022.102965.
[9] W.H. Saputera, A.S. Putrie, A.A. Esmailpour, D. Sasongko, V. Suendo, R.R. Mukti, Technology advances in phenol removals: current progress and future perspectives, Catalysts, 11 (2021) 998, doi: 10.3390/catal11080998.
[10] Yu.V. Sukhatskiy, Z.O. Znak, O.I. Zin, Cavitation and its combinations with other advanced oxidation processes in phenol wastewater treatment: a review, Issues Chem. Chem. Technol. (Voprosy khimii i khimicheskoi technologii), 4 (2020) 16–30, doi: 10.32434/0321-4095-2020-131-4-16-30.
[11] A. Iqbal, E. Cevik, A. Bozkurt, S.M.M. Asiri, O. Alagha, T.F. Qahtan, M.I. Jalees, M.U. Farooq, Ultrahigh adsorption

by regenerable iron-cobalt core-shell nanospheres and their synergetic effect on nanohybrid membranes for removal of malachite green dye, J. Environ. Chem. Eng., 10 (2022) 107968, doi: 10.1016/j.jece.2022.107968.
[12] A. Iqbal, M.I. Jalees, M.U. Farooq, E. Cevik, A. Bozkurt, Superfast adsorption and high-performance tailored membrane filtration by engineered Fe-Ni-Co nanocomposite for simultaneous removal of surface water pollutants, Colloids Surf., A, 652 (2022) 129751, doi: 10.1016/j.colsurfa.2022.129751.
[13] A.M. Girelli, L. Quattrocchi, F.R. Scuto, Design of bioreactor based on immobilized laccase on silica-chitosan support for phenol removal in continuous mode, J. Biotechnol., 337 (2021) 8–17.
[14] L. Yu, D.P. Gamliel, B. Markunas, J.A. Valla, A promising solution for food waste: preparing activated carbons for phenol removal from water streams, ACS Omega, 6 (2021) 8870–8883.
[15] N. Elboughdiri, B. Azeem, D. Ghernaout, S. Ghareba, K. Kriaa, Steam-activated sawdust efficiency in treating wastewater contaminated by heavy metals and phenolic compounds, J. Water Reuse Desalin., 11 (2021) 391–409.
[16] A. Othmani, S. Magdouli, P.S. Kumar, A. Kapoor, P.V. Chellam, Ö. Gökkuş, Agricultural waste materials for adsorptive removal of phenols, chromium(VI) and cadmium(II) from wastewater: a review, Environ. Res., 204 (2022) 111916, doi: 10.1016/j.envres.2021.111916.
[17] Y. Dehmani, O. El Khalki, H. Mezougane, S. Abouarnadasse, Comparative study on adsorption of cationic dyes and phenol by natural clays, Chem. Data Collect., 33 (2021) 100674, doi: 10.1016/j.cdc.2021.100674.
[18] Y. Sun, T. Wang, X. Sun, L. Bai, C. Han, P. Zhang, The potential of biochar and lignin-based adsorbents for wastewater treatment: comparison, mechanism, and application—a review, Ind. Crops Prod., 166 (2021) 113473, doi: 10.1016/j.indcrop.2021.113473.
[19] M.A. Tony, Low-cost adsorbents for environmental pollution control: a concise systematic review from the prospective of principles, mechanism and their applications, J. Dispersion Sci. Technol., 43 (2022) 1612–1633.
[20] T. Wium-Andersen, A.H. Nielsen, T. Hvitved-Jacobsen, N.K. Kristensen, H. Brix, C. Arias, J. Vollertsen, Sorption media for stormwater treatment--a laboratory evaluation of five low-cost media for their ability to remove metals and phosphorus from artificial stormwater, Water Environ. Res., 84 (2012) 605–616.
[21] M. Ahmaruzzaman, Adsorption of phenolic compounds on low-cost adsorbents: a review, Adv. Colloid Interface Sci., 143 (2008) 48–67.
[22] B. Goswami, D. Mahanta, Polyaniline coated nickel oxide nanoparticles for the removal of phenolic compounds: equilibrium, kinetics and thermodynamic studies, Colloids Surf., A, 582 (2019) 123843, doi: 10.1016/j.colsurfa.2019.123843.
[23] A.K.R. Kumar, K. Saikia, G. Neeraj, H. Cabana, V.V. Kumar, Remediation of bio-refinery wastewater containing organic and inorganic toxic pollutants by adsorption onto chitosan-based magnetic nanosorbent, Water Qual. Res. J., 55 (2020) 36–51.
[24] S.M. Moon, H. Min, S. Park, A. Zhexembekova, J.K. Suh, C.Y. Lee, Packaging vertically aligned carbon nanotubes into a heat-shrink tubing for efficient removal of phenolic pollutants, RSC Adv., 9 (2019) 22205–22210.
[25] F. Raposo, C. Ibelli-Bianco, Performance parameters for analytical method validation: controversies and discrepancies among numerous guidelines, TrAC, Trends Anal. Chem., 129 (2020) 115913, doi: 10.1016/j.trac.2020.115913.
[26] S. Naik, C. Nazareth, S. Pereira, A novel HPLC cleaning validation and assay method for the simultaneous estimation of perindopril and amlodipine, Res. J. Pharm. Technol., 13 (2020) 5919–5923.
[27] H.A. Saudi, S.M. Salem, S.S. Mohammad, A.G. Mostafa, M.Y. Hassaan, Utilization of pure silica extracted from rice husk and FTIR structural analysis of the prepared glasses, Am. J. Phys. Appl., 3 (2015) 97–105.
[28] R.K. Sandhu, R. Siddique, Influence of rice husk ash (RHA) on the properties of self-compacting concrete: a review, Constr. Build. Mater., 153 (2017) 751–764.
[29] C. Păcurariu, G. Mihoc, A. Popa, S.G. Muntean, R. Ianoş, Adsorption of phenol and p-chlorophenol from aqueous solutions on poly(styrene-co-divinylbenzene) functionalized materials, Chem. Eng. J., 222 (2013) 218–227.
[30] B. Zeng, W. Xu, S.B. Khan, Y. Wang, J. Zhang, J. Yang, X. Su, Z. Lin, Preparation of sludge biochar rich in carboxyl/hydroxyl groups by quenching process and its excellent adsorption performance for Cr(VI), Chemosphere, 285 (2021) 131439, doi: 10.1016/j.chemosphere.2021.131439.
[31] M.I. Jalees, Synthesis and application of magnetized nanoparticles to remove lead from drinking water: Taguchi design of experiment, J. Water Sanit. Hyg. Dev., 10 (2020) 56–65.
[32] M.I. Jalees, M.U. Farooq, S. Basheer, S. Asghar, Removal of heavy metals from drinking water using Chikni Mitti (kaolinite): isotherm and kinetics, Arabian J. Sci. Eng., 44 (2019) 6351–6359.