

Sorption potential of rice husk for the removal of 2,4-dichlorophenol from aqueous solutions: Kinetic and thermodynamic investigations

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This work is dedicated to our late Prof. Dr. A.W.K. Khanzada, who is not present among us physically, but spiritually he will always remain among us.

Abstract

The sorption potential of chemically and thermally treated rice husk (RHT) for the removal of 2,4-dichlorophenol (DCP) from aqueous solutions has been investigated. Sorption of DCP by rice husk was observed over a wide pH range of 1–10. The effect of contact time between liquid and solid phases, sorbent dose, pH, concentration of sorbate and temperature on the sorption of DCP onto rice husk has been studied. The pore area and average pore diameter of RHT by BET method are calculated to be $17 \pm 0.6 \text{ m}^2 \text{ g}^{-1}$ and $51.3 \pm 1.5 \text{ nm}$, respectively. Maximum sorption ($98 \pm 1.2\%$) was achieved for RHT from $6.1 \times 10^{-5} \text{ mol dm}^{-3}$ of sorbate solution using 0.1 g of rice husk for 10 min agitation time at pH 6 and 303 K, which is comparable to activated carbon commercial (ACC) $96.6 \pm 1.2\%$, but significantly higher than chemically treated rice husk (RHCT) $65 \pm 1.6\%$ and rice husk untreated (RHUT) $41 \pm 2.3\%$. The sorption data obtained at optimized conditions was subjected to Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherms. Sorption intensity $1/n$ (0.31 ± 0.01) and sorption capacity multilayer C_m ($12.0 \pm 1.6 \text{ mmol g}^{-1}$) have been evaluated using Freundlich sorption isotherm, whereas the values of sorption capacity monolayer Q ($0.96 \pm 0.03 \text{ mmol g}^{-1}$) and binding energy, b , (4.5 ± 1.0) $\times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ have been estimated by Langmuir isotherm. The Langmuir constant, b , was also used to calculate the dimensionless factor, R_L , in the concentration range $(0.6\text{--}6.1) \times 10^{-4} \text{ mol dm}^{-3}$, suggesting greater sorption at low concentration. D–R sorption isotherm was employed to calculate sorption capacity X_m ($2.5 \pm 0.07 \text{ mmol g}^{-1}$) and sorption energy E ($14.7 \pm 0.13 \text{ kJ mol}^{-1}$). Lagergren and Morris–Weber equations were employed to study kinetics of sorption process using 0.2 g of RHT, 25 cm^3 of $0.61 \times 10^{-4} \text{ mol dm}^{-3}$ sorbate concentration at pH 6, giving values of first-order rate constant, k , and rate constant of intraparticle transport, R_{id} , ($0.48 \pm 0.04 \text{ min}^{-1}$ and $6.8 \pm 0.8 \text{ nmol g}^{-1} \text{ min}^{-1/2}$, respectively) at $0.61 \times 10^{-4} \text{ mol dm}^{-3}$ solution concentration of DCP, 0.1 g RHT, pH 6 and 2–10 min of agitation time. For thermodynamic studies, sorption potential was examined over temperature range 283–323 K by employing $6.1 \times 10^{-4} \text{ mol dm}^{-3}$ solution concentration of DCP, 0.1 g RHT at pH 6 and 10 min of agitation time and values of ΔH ($-25 \pm 1 \text{ kJ mol}^{-1}$), ΔS ($-61 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$) and $\Delta G_{303\text{K}}$ ($-7.1 \pm 0.09 \text{ kJ mol}^{-1}$) were computed. The negative values of enthalpy, entropy, and free energy suggest that the sorption is exothermic, stable, and spontaneous in nature.
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Keywords: Rice (*Oryza sativa*) husk; 2,4-Dichlorophenol; Sorption potential; HPLC; Kinetics; Thermodynamics

1. Introduction

Contamination of ground and surface water by different organic pollutants is a major factor of environmental problems for the number of years. Among these organic pollutants, chlorophenols are most common and have been highlighted as priority pollutants by Stringent US Environmental

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Protection Agency (EPA) [1,2]. These pollutants are discharged by the industries into natural water streams and contaminate the ground water [3]. Many of these compounds enter into wastewaters from petrochemical, coal tar, plastic and pesticidal chemical industries, which produce them as chemical intermediates or generate them during chlorination of effluents containing phenolic compounds [4–6]. Industrial wastewater is not the only source of phenols; rather they could be present in domestic waters since they are widely used as pesticides, disinfectants, antiseptics, pharmaceuticals, dyes and cosmetics [7,8]. In addition, common water treatment with chlorine could generate chlorophenols, since chlorine reacts quite rapidly with phenols [9].

The presence of these compounds in different industrial effluents often represents a risk to the environment [10,11]. They are toxic to most aquatic organisms, human body and may cause denaturing of protein, tissue erosion, paralysis of the central nervous system and also damage the kidney, liver and pancreas [12,13]. They are toxic even at very low concentrations. So, it is recommended to decrease their concentration up to 0.1 mg/l in wastewaters, if complete removal is not possible before their discharge into water streams [3].

Different methods, such as chemical oxidation, coagulation, chlorination, solvent extraction, liquid membrane permeation and adsorption, have previously been employed for removal of these pollutants from different water systems [14].

Adsorption is a commonly utilized method for the treatment of various industrial effluents. Different authors have reported the adsorption of phenols on activated carbon from wastewaters [15,16]. But its high cost inhibits its application on large scale, being very expensive to purchase, regeneration leads to the production of additional contaminants. Due to these problems, investigation of some new, indigenous and cheaper sorbents for the removal of these contaminants is focus of intense research now a days. Adsorption on indigenous materials is a relatively simple and inexpensive method for the treatment of industrial and domestic effluents [17–19]. Number of cheaper materials, including industrial and agricultural wastes, have been used to remove different pollutants from industrial effluents for their safe disposal into the biosphere. Atsuko et al. [20] reported rice bran to be a potent sorbent for the removal of organochlorine compounds and benzene from industrial wastewaters. Hasany and Chaudhary [21] employed river sand for sorption of cadmium(II) from aqueous solutions; Nakbanpote et al. [22] used rice husk ash for preconcentration of gold. Similarly, Tutem et al. [23] and Mogyorosi et al. [24] exploited bituminous shale and hydrophobic clay for the removal of chlorophenols and 2-chlorophenol as effective sorbents. Efficiency of sorbent is mainly dependent on surface area and binding forces present within the particles of sorbent, as well as chemical characteristics of sorbate.

Rice husk is a by-product of milling process of rice crop, which is widely cultivated in Asian countries. It is used in fodder of animals or discarded as agricultural waste, as it is abundantly available. Maximum cost of commercially available rice husk is ~40 kg/US \$. Major components of rice husk which may be responsible for sorption are carbon and silica [22,25]. Silica is composed of $\text{SiO}_4 \cdot 4\text{H}_2\text{O}$ in which each oxygen atom is shared between two adjacent tetrahedrons. The Si–O bond is about 50% ionic owing to the large difference in the electronegativity of oxygen and silicon. Thus, the ionic structure of silica provides a capability of adsorbing phenolic compounds which are polar molecules [26]. No detailed information about sorption potential of rice husk from Pakistani varieties has been published. Previously reported work on sorption potential of rice husk by some authors is insufficient [27]. No kinetic and thermodynamic discussions of sorption data have been presented so far. In this report, a detailed study on sorption potential of rice husk has been presented. Data have been explained on the basis of kinetic and thermodynamic models.

2. Experimental

2.1. Reagents and materials

All the reagents were of analytical grade and procured from Fluka Chemical Co. or E. Merck, Germany. DCP of 99.9% purity was obtained from Sigma Chemicals Ltd., USA. Methanol (HPLC grade) was procured from Merck, Germany, and used for making synthetic aqueous solutions and for HPLC method. Activated carbon commercial was procured from Wako Pure, Chemicals Industries Ltd., Japan. All glasswares used were of Pyrex, Germany. Throughout the experiments, all glasswares were cleaned with 20% nitric acid and repeatedly washed with deionized water, followed by drying at 383 K in an oven for 5 h.

Stock solution of DCP was prepared by dissolving 1 g (appropriate volume from mass density ratio) of 2,4-dichlorophenol (DCP) in 10 cm³ of methanol, and then volume was made up to 1000 cm³ with doubly distilled deionized water. The samples of required concentrations were prepared by diluting the stock solution of DCP. The buffers of pH (1–3), (4–6) and (7–10) were prepared by mixing an appropriate volume of 0.1 M solutions of HCl–KCl, CH₃COOH–CH₃COONa and H₃BO₃–NaOH, respectively [28].

2.2. Preparation of sorbent

Rice (*Oryza sativa*) husk from an indigenous variety super kernel basmati was purchased from local rice milling plant, washed thoroughly with doubly distilled deionized water to avoid the presence of foreign impurities and dried in sunlight for 8 h. The washed and dried material was sieved to different mesh sizes from 200 to 400 μm in Ro-Tap type electrical

Table 1
The % chemical composition of RHT with X-ray fluorescence (XRF) analysis

SiO ₂	95.1 ± 0.6
CaO	0.28 ± 0.05
MgO	0.14 ± 0.06
K ₂ O	0.13 ± 0.05
MnO	0.03 ± 0.001

sieve shaker. Average particle size of 300 μm was chosen for present work. The sieved material (500 g) was rewashed thoroughly with doubly distilled deionized water to remove the fine particles and dried at 383 K for 4 h in an oven; a (100 g) portion of this dried rice husk was placed in vacuum desiccator to be used directly as sorbent (RHUT). While 200 g portion of the same dried rice husk was chemically treated with 0.1 M nitric acid for 1 h, followed by soaking in methanol for 4 h (RHCT) to remove inorganic and organic matter from the surface of rice husk. One-hundred gram portion of chemically treated rice husk was subjected to thermal treatment in a closed muffle furnace (Phoenix, Sheffield, England, 1983) at 573 K for 1 h (RHT) to increase the surface area [29], while other fraction (50 g) of chemically treated rice husk (RHCT) was used directly as sorbent to estimate the differences of sorption due to thermal treatment. The ash form of thermally treated rice husk (RHT) was used as sorbent. The chemical composition of RHT was determined by X-ray fluorescence (XRF) analysis (Table 1).

2.3. Instrumentation

Hitachi model 6200 HPLC equipped with a Licosorb ODS column 5 μm (Ø 150 mm × 4 mm) UV–Vis detector equipped with a CSW32 software, was used for data acquisition, integration and processing. Doubly distilled deionized water (with 0.8 μS cm⁻¹ conductance, 5.8 pH) and methanol (20:80) were used as mobile phase at a flow rate of 1 ml/min, arbitrary unit full scale deflection (AUFS) 0.005 and at 254 nm wavelength. The limit of detection (signal to noise ratio 2) was observed to be 0.05 ng μl⁻¹ for 2,4-DCP. The pH measurements were made on digital (Inolab level 1) pH meter, Germany.

2.4. Removal method

Appropriately weighed sorbent (0.025–1.0 g) was placed in dry conical flasks to which 25 cm³ of sorbate containing varying amount of analyte (0.61–6.0) × 10⁻⁴ mol dm⁻³ was added. The flasks were then fitted to a Gallenkamp No. 350–010 thermostatic shaker at a speed of 100 rpm (revolution/min) at 303 ± 2 K for 2–20 min. Blank sample was simultaneously placed in the same shaker. Finally, the sample was filtered using Whatmann filter paper no. 44. A 10 μl of sample solution was then injected to HPLC under optimized conditions. The sorbed concentration of sorbate on sorbent surface was calculated by the difference in the detec-

tor response peak height (mV) before and after shaking. The % sorption and distribution coefficient were calculated by Eqs. (1) and (2), respectively, as follows:

$$\% \text{ Sorption} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

$$R_d = \frac{\text{Amount of analyte in rice husk}}{\text{Amount of analyte in solution}} \times \frac{V}{W} \quad (2)$$

where C_i and C_e are the initial and equilibrium concentrations (mol dm⁻³), respectively, of sorbate; R_d is the distribution coefficient; V is the volume of the solution (cm³); and W is the weight of rice husk (g).

Correlation among % sorption and the distribution coefficient may be located by the following equation:

$$\% \text{ Sorption} = \frac{100R_d}{R_d + (V/W)} \quad (3)$$

All the experiments were performed in triplicate. The linear regression computer program with one independent variable was used for slope and statistical analyses of the data [30].

3. Results and discussion

Sorption is a surface phenomenon and is affected significantly by physical and chemical characteristics of sorbent and sorbate. Sorption studies on rice husk were carried out by optimizing various parameters, i.e. effect of agitation time, amount of sorbent, pH, concentration of sorbate and temperature.

3.1. Effect of thermal treatment

Effect of thermal treatment on the sorption potential of rice husk was studied by employing 0.5 g RHCT, 25 cm³ of 0.61 × 10⁻⁴ mol dm⁻³ solution concentration of DCP, 8 min of agitation time at pH 6 and 100 rpm shaking speed. The results are portrayed in Fig. 1. Before thermal treatment,

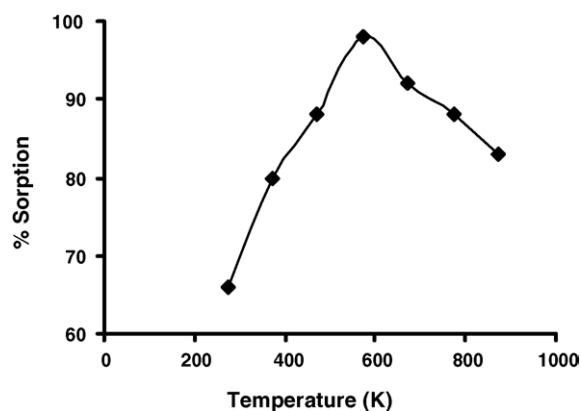


Fig. 1. Effect of thermal treatment on % sorption of DCP onto rice husk.

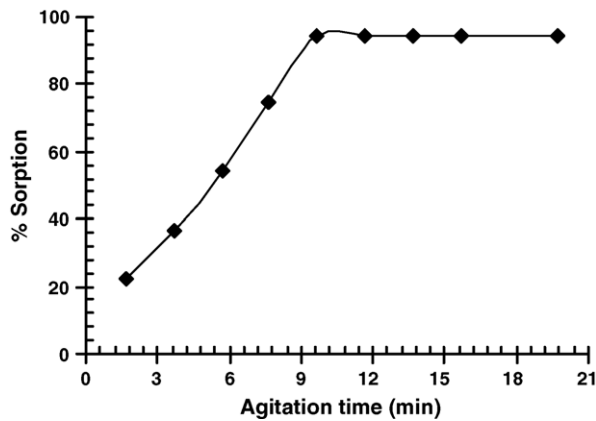


Fig. 2. Effect of agitation time on % sorption of DCP onto rice husk.

RHCT (at 273 K) has sorption potential 66%, which increases regularly and sharply up to 98% when temperature of furnace increases (573 K), followed by a regular, gradual but relatively less sharp decrease (up to 873 K). Increase in sorption potential of rice husk by increasing temperature of furnace from 273 to 573 K was approximately 32%, while decrease in sorption potential (15%) at higher temperature from 673 to 873 K may be due to some structural changes at the surface of rice husk. For further studies, thermally treated rice husk at 573 K (RHT) was selected as a sorbent.

3.2. Effect of shaking time

Effect of shaking time on % sorption of DCP onto rice husk was studied over an agitation time of 2–20 min, using 0.2 g of RHT, 25 cm³ of 0.61×10^{-4} mol dm⁻³ sorbate concentration at pH 6, temperature 303 K and 100 rpm shaking speed. The results are depicted in Fig. 2. Percent sorption increases from 26 to 97% at contact time of 10 min. This represents the time at which equilibrium of DCP concentration is presumed to have been attained. The equilibrium time for DCP calculated from this study is far less than that reported for phenol onto rice husk, i.e. 120 min [31].

3.3. Effect of sorbent dosage

Fig. 3 indicates the effect of amount of sorbent on % sorption of 2,4-dichlorophenol. Amount of sorbent was optimized at 10 min of agitation time by using 0.025–1 g of sorbent, 25 cm³ of 0.61×10^{-4} mol dm⁻³ of sorbate concentration at pH 6 and 100 rpm shaking speed and reaction temperature of 303 K. Percent sorption increases very rapidly up to 66% by increasing amount of the sorbent from 0.025 to 0.1 g and stays almost constant up to 1 g of sorbent dosage. Previous reports clearly reveal that there should be a ratio between sorbent dose and sorbate concentration, which represent maximum % sorption [28].

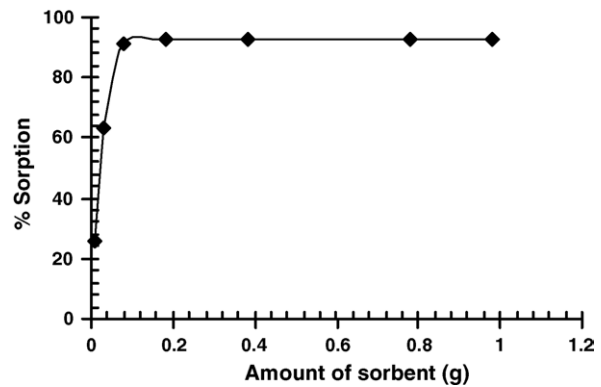


Fig. 3. Influence of amount of rice husk on the % sorption of DCP.

3.4. Effect of pH

Fig. 4 depicts the effect of pH on % sorption of DCP onto rice husk. Optimization of pH of sorption medium plays vital role in the sorption studies. Effect of pH was studied in the pH range 1–10 with optimized 0.1 g sorbent dose, 10 min of agitation time, 25 cm³ of 6.1×10^{-4} mol dm⁻³ sorbate concentration and at temperature 303 K. Percent sorption of DCP onto rice husk was found higher at low pH. At lower pH values, chlorinated phenols are present as the neutral phenols. The more percent sorption of 76% at pH 1.0 may be the result of the strong chemical bonding between the lone pair of electrons present on the –OH group in chlorinated phenols and the Si⁴⁺ of the rice husk [32]. The chloride (–Cl) ion on the benzene ring, which increases the acidic character is responsible for forming anion on the oxygen atom of the –OH group and also has a strong affinity for silica surfaces [22]. At a lower pH, there is a reasonably strong interaction between the sorbent and the polar resonance contributed phenol structure. Besides this, chances of hydrogen bonding by the phenolic protons with the oxygen present on the silica surface cannot be ignored.

Furthermore, a comparative study was carried out for estimating the sorption potential of RHUT, RHCT, RHT and ACC at optimized conditions of 0.1 g of each sorbent, 10 min

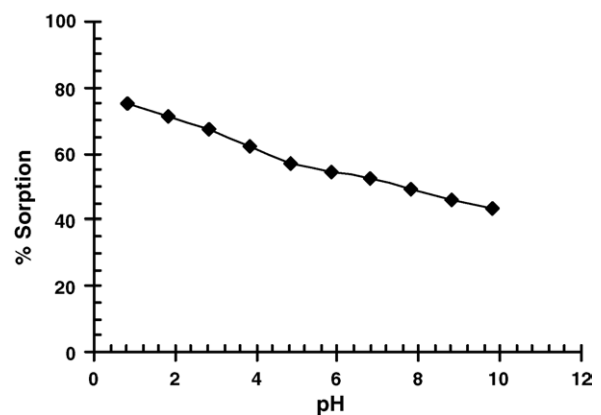


Fig. 4. Effect of pH on % sorption of DCP onto rice husk.

Table 2
Physical properties of sorbents and their % sorption for DCP

Sorbents	Average particle size (μm)	Pore area ($\text{m}^2 \text{g}^{-1}$)	Average pore diameter (nm)	% Sorption of sorbents ^a
RHUT	300	11 ± 0.8	40 ± 2.2	41 ± 2.3
RHC	300	14 ± 0.5	46 ± 1.8	65 ± 1.6
RHT	300	17 ± 0.6	51 ± 1.5	98 ± 1.2
ACC	5	755 ± 12	0.6 ± 0.05	96.6 ± 1.2

^aSorbents (RHUT, RHCT, RHT and ACC).

contact time, pH 6, 25 cm^3 of $0.61 \times 10^{-4} \text{ mol dm}^{-3}$ solution concentration of DCP and temperature of 303 K. The results are listed in Table 2.

3.5. Sorption dynamics

Fig. 5 shows the kinetic study of sorption of DCP onto rice husk at conditions chosen while investigating effect of agitation time on % sorption of DCP onto rice husk. The rate constant of sorption is determined from the first-order rate expression given by the Lagergren equation [33].

$$\log(q_e - q_t) = \log q_e - \frac{kt}{2.303} \quad (4)$$

$\log(q_e - q_t)$ was plotted versus agitation time resulting in a straight line with coefficient of determination, R^2 , (0.9791 ± 0.11009). The q_e and q_t are the equilibrium and sorbed concentrations, respectively, at time, t , and the value of k , the first-order rate constant, computed from the slope of the linear plot as $0.48 \pm 0.04 \text{ min}^{-1}$.

The kinetics of sorption of DCP was also examined using Morris–Weber equation [34] in the following form:

$$q_t = R_{id}\sqrt{t} \quad (5)$$

where q_t is the sorbed concentration at time ' t ', and R_{id} is the rate constant of intraparticle transport. The q_t was plotted against, $t^{1/2}$ in Fig. 6. The sorption data follow linearity as per Eq. (5) up to 10 min with coefficient of determination, R^2 , (0.9604 ± 0.0011). The value of R_{id} computed from the slope of the plot comes out $6.8 \pm 0.8 \text{ nmol g}^{-1} \text{ min}^{-1/2}$.

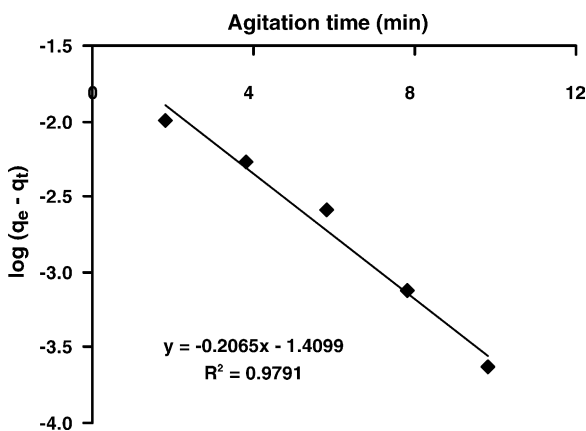


Fig. 5. Lagergren plot of DCP onto rice husk.

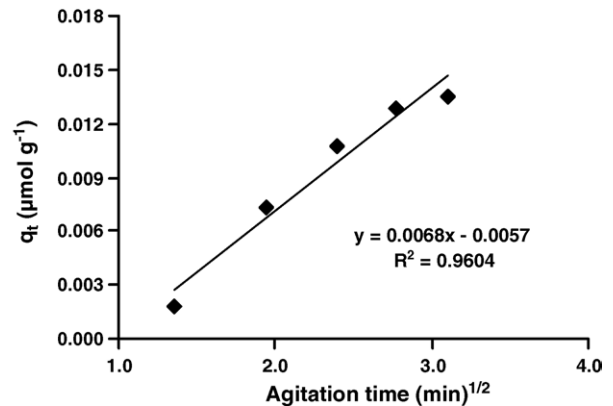


Fig. 6. Validation of Morris–Weber equation for DCP onto rice husk.

3.6. Effect of DCP concentration (mol dm^{-3}) on its sorption onto RHT

The effect of DCP concentration on its sorption onto rice husk was studied over concentration range of $0.61\text{--}6.1 \times 10^{-4} \text{ mol dm}^{-3}$ using optimized conditions mentioned above (Fig. 7). It was found that the distribution coefficient, R_d , decreases with the increase in DCP concentration up to $4 \times 10^{-4} \text{ mol dm}^{-3}$ with a gradual fall resulting in slope, and becomes almost constant from $4\text{--}6 \times 10^{-4} \text{ mol dm}^{-3}$ of DCP solution. This may be interpreted in terms of limiting sorption sites, which may not be sufficient to accommodate increasing number of 2,4-dichlorophenol molecules available onto sorbent surface.

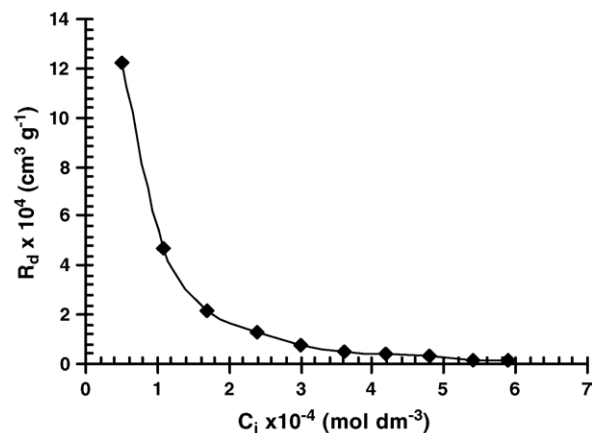


Fig. 7. Effect of concentration of DCP on its sorption onto rice husk.

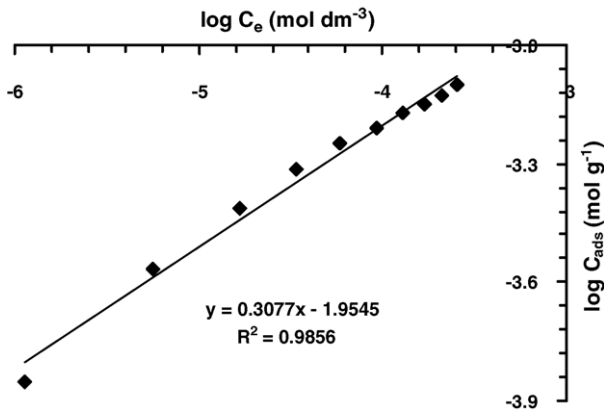


Fig. 8. Freundlich sorption isotherm of DCP onto rice husk.

3.7. Modeling of sorption isotherms

The sorption isotherms express the specific relation between the concentration of sorbate and its degree of accumulation onto sorbent surface at constant temperature. The sorption capacities of rice husk for DCP have been evaluated using different isotherms, namely Freundlich, Langmuir and Dubinin–Radushkevich (D–R) employing data shown in Fig. 7.

3.8. Freundlich sorption isotherm

Fig. 8 shows Freundlich sorption isotherm of DCP onto rice husk. It is the most widely used empirical expression that accounts for the surface heterogeneity, exponential distribution of active sites of sorbent and their energies towards sorbate [35]. Although it does not take the solids finite capacity for sorption at high concentration of the solute into account, it can describe the experimental data well on a phenomenological basis. The linearized form of Freundlich isotherm is tested in the following form:

$$\log C_{\text{ads}} = \log C_m + \frac{1}{n} \log C_e \quad (6)$$

where $1/n$ is a characteristic constant related to sorption intensity, C_{ads} is the sorbed concentration of sorbate onto sorbent (mol g^{-1}), C_e represents equilibrium concentration of sorbate in solution, and C_m is the multilayer sorption capacity of sorbent (mol g^{-1}). Logarithmic plot of sorbed and equilibrium concentration gives a straight line with coefficient of determination close to unity (0.9856 ± 0.03012). The values of $1/n$ (0.31 ± 0.01) and C_m ($12.0 \pm 1.6 \text{ mmol g}^{-1}$) are derived from the slope and intercept of the straight line, respectively.

3.9. Langmuir isotherm

Fig. 9 shows the simplest theoretical model for monolayer sorption, i.e. Langmuir isotherm [36] of DCP onto rice husk. The Langmuir model was originally developed to represent

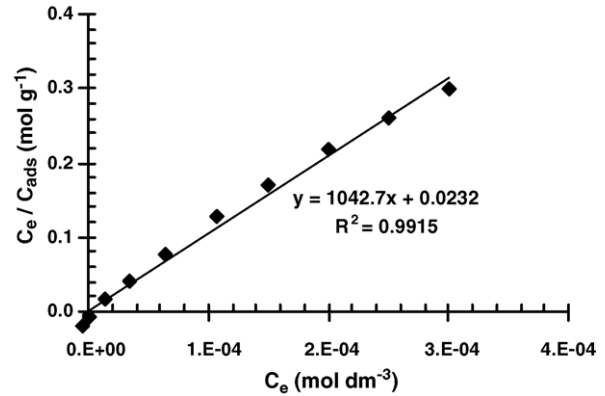


Fig. 9. Langmuir sorption isotherm of DCP onto rice husk.

monolayer sorption on a set of distinct localized sorption sites. It gives uniform energies of monolayer sorption onto sorbent surface with no transmigration of sorbate in the plane of the surface. There are no interactions between the sorbed molecules, no steric hindrance between sorbed molecules and incoming ions, and all the sorption sites are alike and uniform on microscopic scale. The sorption data is also applied to the following linearized form of Langmuir isotherm:

$$\frac{C_e}{C_{\text{ads}}} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (7)$$

where Q is the monolayer sorption saturation capacity (mol g^{-1}), and b represents the enthalpy of sorption ($\text{dm}^3 \text{ mol}^{-1}$), independent of temperature. In Fig. 9, C_e/C_{ads} is plotted against C_e yielding a straight line with R^2 (0.9915 ± 0.0112), indicating that sorption data fit well into the Langmuir model. The value of Q ($0.96 \pm 0.03 \text{ mmol g}^{-1}$) was calculated from the slope of the linear plot, whereas the value of b ($4.5 \pm 1.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$) was derived from the intercept [37].

From the value of b , a dimensionless parameter, R_L [38], was estimated in the concentration range $(0.6\text{--}6.1) \times 10^{-4} \text{ mol dm}^{-3}$, using the relationship:

$$R_L = \frac{1}{1 + bC_i} \quad (8)$$

where b is the Langmuir constant ($\text{dm}^3 \text{ mol}^{-1}$) and C_i is the initial concentration (mol dm^{-3}).

The value of R_L in the range 0.04–0.27 indicates that sorption is higher at low concentration.

3.10. Dubinin–Radushkevich (D–R) isotherm

Fig. 10 shows the Dubinin–Radushkevich (D–R) isotherm model [39]. It is also applied to the sorption data in the following linearized form:

$$\ln C_{\text{ads}} = \ln X_m - \beta \varepsilon^2 \quad (9)$$

where C_{ads} is the amount of sorbate sorbed onto sorbent surface (mol g^{-1}) and X_m represents the maximum sorption

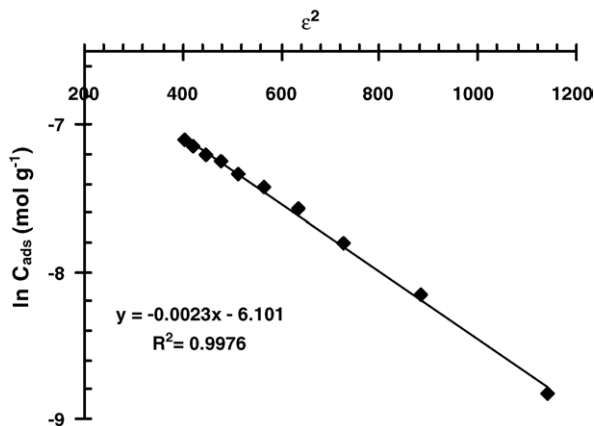


Fig. 10. D–R sorption isotherm of DCP onto rice husk.

capacity of sorbent (mol g^{-1}), β is constant related to sorption energy, while ε is Polanyi sorption potential which is equal to:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (10)$$

R is a gas constant in $\text{kJ mol}^{-1} \text{K}^{-1}$, T is the temperature in Kelvin, and C_e is the equilibrium concentration of sorbate in solution (mol dm^{-3}). The Polanyi sorption theory [40] postulates fixed volume of sorption sites close to the sorbent surface and existence of sorption potential over these sites. Polanyi sorption potential, ε is the work required to remove a molecule to infinity from its location in the sorption space, independent of temperature. This model assumes the heterogeneity of sorption energies within this space. The plot of $\ln C_{\text{ads}}$ versus ε^2 is a straight line with coefficient of determination, R^2 , (0.9976 ± 0.02827). The computed value of β and X_m from the slope and intercept are $-0.0023 \pm 0.00004 \text{ kJ}^2 \text{ mol}^{-2}$ and $2.5 \pm 0.07 \text{ mmol g}^{-1}$, respectively. The value of sorption energy, E , can be correlated to β using the following relationship [41]:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (11)$$

The value of E for DCP calculated from Eq. (11) is $14.7 \pm 0.13 \text{ kJ mol}^{-1}$.

3.11. Effect of temperature

The effect of temperature, a major factor influencing the sorption, was monitored in the range of 283–323 K under the optimized conditions chosen. The plot of $\ln K_c$ versus $1/K$ gives a straight line with coefficient of determination ' R^2 ' (0.9917 ± 0.05566) as shown in Fig. 11.

$K_c = F_e / (1 - F_e)$, where F_e is the fraction sorbed at equilibrium, while K is the temperature in kelvin. The thermodynamic parameters, such as enthalpy ΔH , entropy ΔS , and Gibbs free energy ΔG were estimated [42,43] using follow-

Table 3
Physio-chemical characteristics of phenolic wastewater

S. no.	Characteristics	Values
1	pH	7.3
2	EC ($\mu\text{S cm}^{-1}$)	286
3	Sulphate (mg l^{-1})	58
4	Chloride (mg l^{-1})	54
5	TDS (mg l^{-1})	234
6	COD (mg l^{-1})	485
7	BOD (mg l^{-1})	59
8	DCP ($\mu\text{g ml}^{-1}$)	1.5

ing equations:

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (12)$$

$$\Delta G = -RT \ln K_c \quad (13)$$

From the slope and intercept of plot, the values of ΔH ($-25 \pm 1 \text{ kJ mol}^{-1}$) and ΔS ($-61 \pm 4 \text{ J mol}^{-1} \text{K}^{-1}$) have been computed, while ΔG is calculated using Eq. (13). The results are presented in Table 3. It may be deduced from the negative values of ΔH and ΔG that the sorption process is exothermic and spontaneous with weak bond formation between sorbate and sorbent. The decrease in the value of ΔG with the increase of temperature shows that the reaction is more spontaneous at high temperature (Table 3). The negative value of ΔS shows the stability of sorption process with no structural change at solid–liquid interface.

3.12. Column method

For determining the suitability of adsorbent and eluting solvent, the % recovery of the 2,4-dichlorophenol was investigated using a glass column ($\text{Ø } 30 \text{ cm} \times 0.7 \text{ cm}$) containing 0.1 g of rice husk on a glass wool support. The column was loaded with 500 ml of $0.61 \times 10^{-4} \text{ mol dm}^{-3}$ of DCP solution, for 2 h at a flow rate of 4.17 ml/min. More than 99% of DCP was sorbed on the sorbent surface. The elution of sorbed DCP was carried out with 6 ml each of methanol, NaOH (0.5 M), HCl (0.1 M) and doubly distilled deionized water by sonication in an ultrasonic bath for 10 min (Fig. 11).

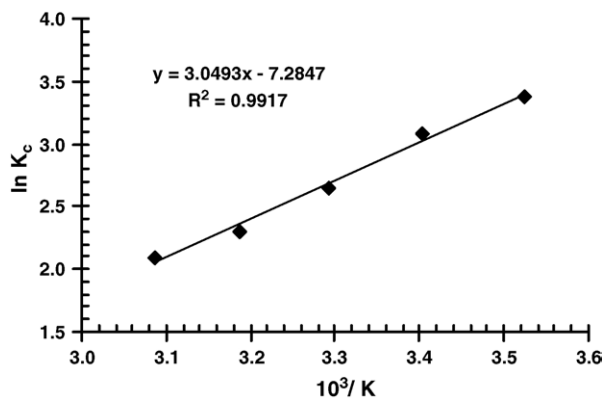


Fig. 11. Variation of sorption equilibrium of DCP onto rice husk with temperature.

Table 4

Thermodynamic constant ΔG calculated for sorption of 2,4-DCP onto rice husk

S. no.	Temperature (K)	ΔG (kJ mol ⁻¹)
1	283	-8.2 ± 0.030
2	293	-7.8 ± 0.029
3	303	-7.1 ± 0.028
4	313	-6.2 ± 0.027
5	323	-5.9 ± 0.026

The elution capacity as % recovery of 2,4-dichlorophenol followed the order as:

MeOH (99 ± 0.5%) > NaOH (90 ± 1%) > HCl (11 ± 2%)
> H₂O (4 ± 2%)

4. Application

4.1. Removal of phenol from industrial wastewater

Industrial wastewater sample (5 l) was collected in a brown glass collection bottle with Teflon-lined caps directly from the outlet of a pharmaceutical and paper mill (phenolic-based industry) located at Petaro Road, Jamshoro, Pakistan, during operation of the plant, and its physio-chemical characteristics are listed in Table 4. The sample was immediately brought to the laboratory to be placed in deep freezer at a temperature of -6 °C. Before analysis, the sample is filtered with Whatmann filter paper No. 44 and kept for further usage. 1 litre of the filtered sample was spiked with 10 mg of DCP. 10 µl (from 500 ml portion of the spiked sample) was then injected to HPLC for further analysis. By comparison of the retention time and peak height (mV) with synthetic sample solution, 1.5 ± 0.04 µg ml⁻¹ of DCP was found to be present in the industrial wastewater. Another 500 ml aliquot of spiked wastewater was then treated with 0.1 g of rice husk as per column method discussed. Rice husk effectively removes 99 ± 0.2% of 2,4-dichlorophenol from wastewater. The sorbed amount of DCP was recovered with 6 ml of methanol and the percent recovery was found to be 99 ± 0.6%.

5. Conclusion

Maximum sorption of 2,4-dichlorophenol is achieved at a concentration of 0.61 × 10⁻⁴ mol dm⁻³. The values of 1/n and R_L from Freundlich and Langmuir isotherms reveal better sorption at low concentrations. Results of sorption energy obtained from D-R isotherm shows the physisorption nature of the sorption process. The negative values of ΔS show the stability of the sorption process, whereas the results of ΔH and ΔG indicate the exothermic and spontaneous nature of the sorption process on the surface of rice husk. Result of Lagergren plot follows first-order rate equation. Methanol

was found to be more suitable solvent for desorption of the sorbate. The desorbed DCP can be used as a raw material in different industries. Elemental analysis of RHT (Table 2) shows that SiO₂ is the main component of rice husk. Rice husk, effectively removes DCP from water and wastewater, is inexpensive, indigenous and easily available in large quantity, and its use as sorbent would significantly lower the cost of wastewater treatment.

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